

	Type	L #	Hits	Search Text	DBs	Time Stamp
1	IS&R	L2	6951	(("29/889.1") or ("29/889.7") or ("29/527.2") or ("29/402.09") or ("29/402.11") or ("29/402.13") or ("29/402.18") or ("427/453") or ("427/456") or ("427/376.2-376.8") or ("228/119") or ("228/193") or ("228/194") or ("219/121.36") or ("219/121.47")).CCLS.	USPAT; EPO; JPO; DERWEN T; IBM TDB	2001/04/06 14:40
2	BRS	L3	54	2 and (hot adj isostatic adj pressing or HIP) and (thermal adj coating or spray)	USPAT; EPO; JPO; DERWEN T; IBM TDB	2001/04/06 15:24
3	BRS	L6	11	2 and (hot adj isostatic adj pressing or HIP) and (spray adj coating) and (sintering)	USPAT; EPO; JPO; DERWEN T; IBM TDB	2001/04/06 15:31

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1			0
2			0
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US005156321A

**United States Patent** [19]

Liburdi et al.

[11] Patent Number: **5,156,321**[45] Date of Patent: **Oct. 20, 1992****[54] POWDER METALLURGY REPAIR TECHNIQUE**

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[73] Assignee: **Liburdi Engineering Limited, Canada**

[21] Appl. No.: **572,582**

[22] Filed: **Aug. 27, 1990**

[51] Int. Cl.<sup>5</sup> ..... **B23P 6/04; B23K 31/02**

[52] U.S. Cl. .... **228/119; 228/175; 228/176; 228/239; 228/248; 29/889.1**

[58] Field of Search ..... **228/119, 175, 176, 239, 228/248; 164/97, 108; 29/530, 402.18, 889.1; 419/8, 9, 27**

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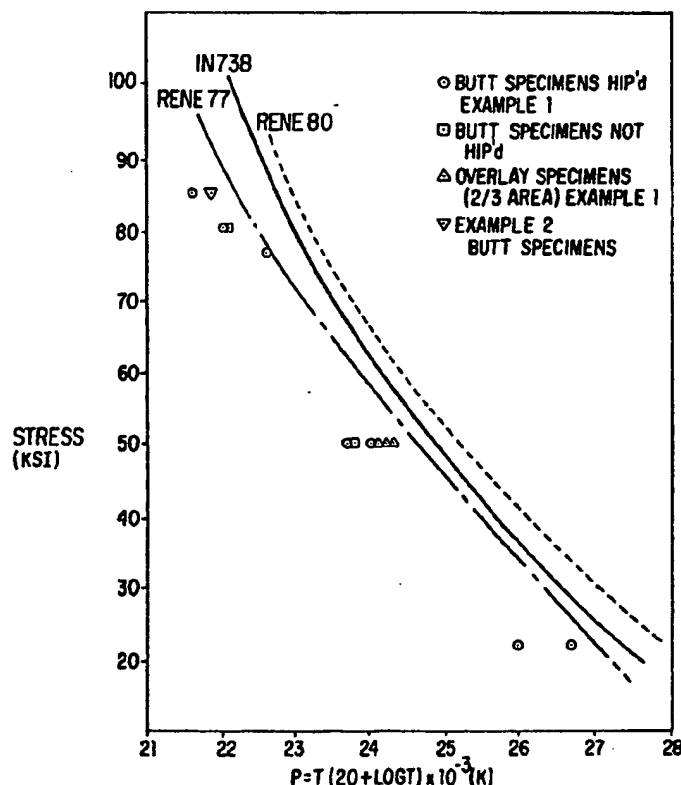
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*Primary Examiner*—Samuel M. Heinrich

*Attorney, Agent, or Firm*—Morgan & Finnegan

**[57] ABSTRACT**

To repair or join sections of a metal article, matching metal powder is sintered in the solid state to form a porous structure in the joint. A layer of matching powder, modified to incorporate melting point depressants such as boron and silicon is subsequently added to the surface of the sintered region. The joint is processed at a temperature where the modified layer melts while the sintered layer and base metal remain solid. The modified material flows into the sintered layer by capillary action and promotes liquid phase sintering, resulting in a dense joint with properties approaching those of the base metal.

**20 Claims, 8 Drawing Sheets**

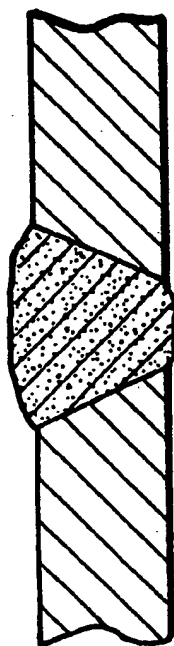


FIG. 1B



FIG. 1A

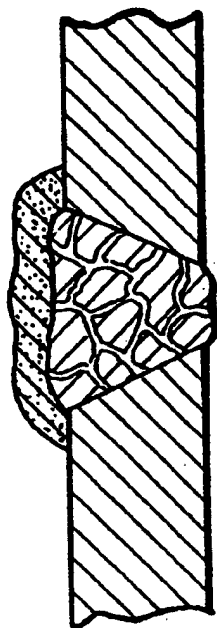


FIG. 1D

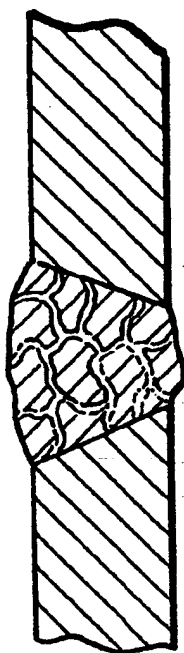


FIG. 1C

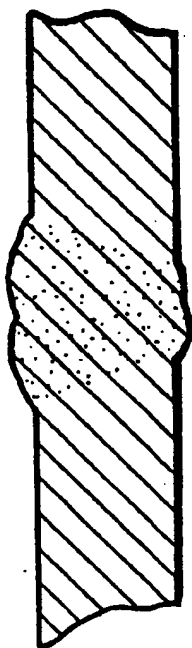


FIG. 1F

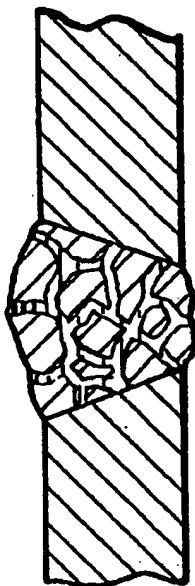


FIG. 1E

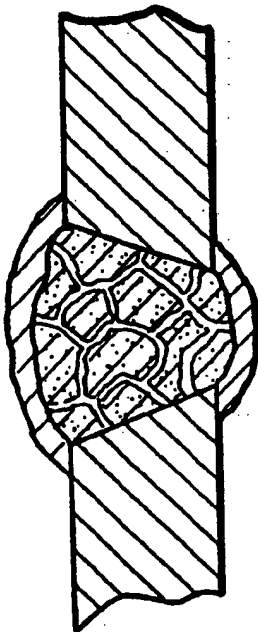


FIG. 2B

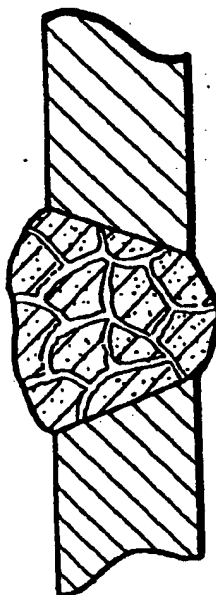


FIG. 2A

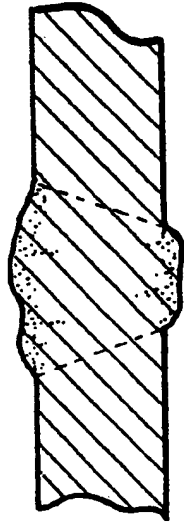


FIG. 2C

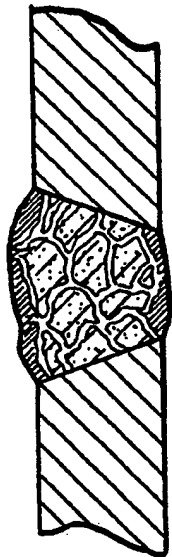


FIG. 2D

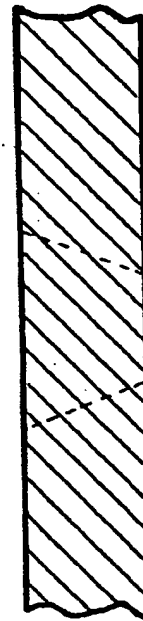


FIG. 2E

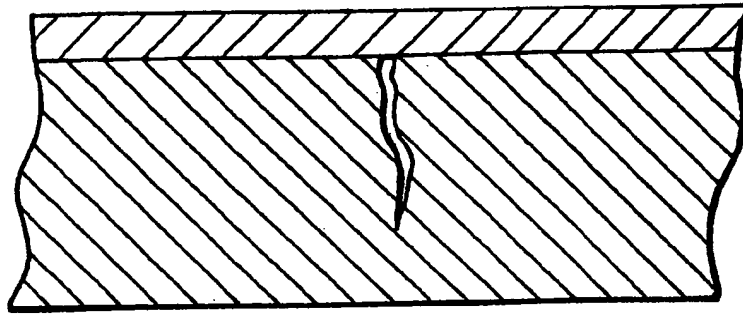


FIG. 3A

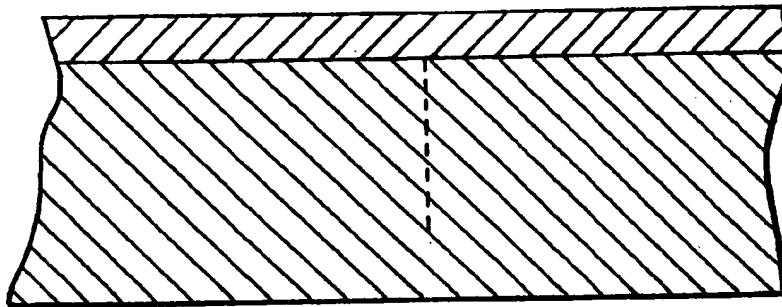


FIG. 3B

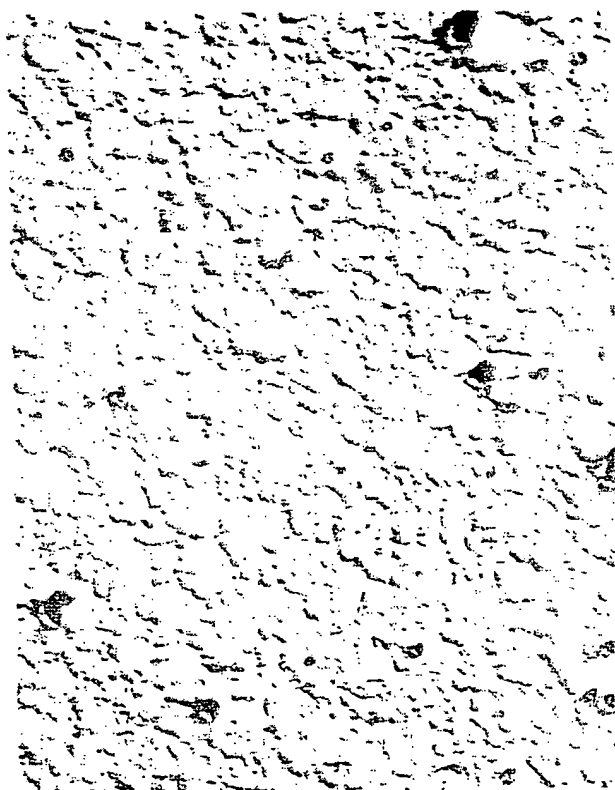


FIG. 4

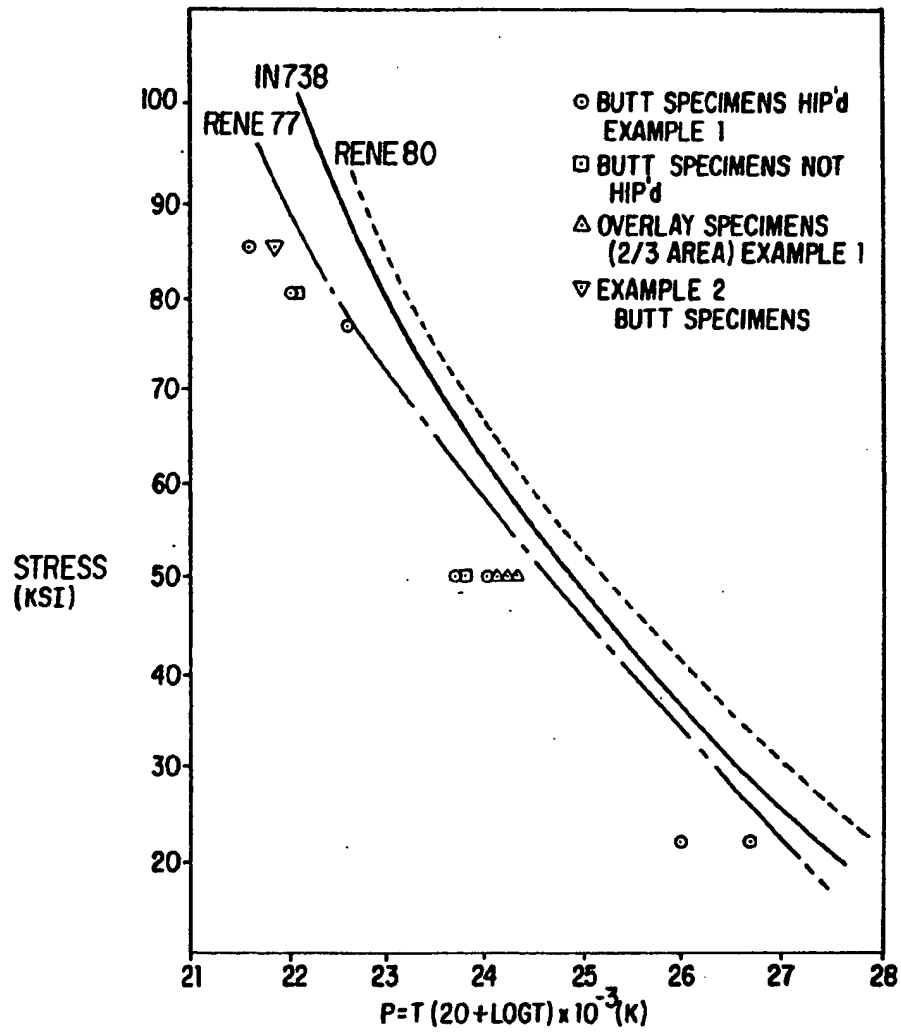


FIG. 5

## POWDER METALLURGY REPAIR TECHNIQUE

### FIELD OF THE INVENTION

This invention relates to the repair or joining of metallic materials and more specifically, to the repair of nickel, iron or cobalt-based superalloy articles.

### BACKGROUND OF THE INVENTION

Components for gas turbine engines manufactured from nickel and cobalt-based superalloys often contain defects from manufacturing or service. Because these components are costly, there is considerable incentive to repair them. However, due to the lack of suitable repair procedures, many parts are currently scrapped. The use of fabricated superalloy components is similarly limited by the absence of suitable joining techniques.

Several repair techniques have been previously developed and are currently being used in specific applications. Fusion welding of superalloys is difficult due to their tendency to form weld-related cracks. Thamburaj, et al., *Int. Met. Rev.*, Vol. 28, No. 1, pp. 1-22 (1983). However, welding is possible using lower strength filler materials. Unfortunately, this limits the use of welding to low stressed areas.

Brazing is also commonly used to join or repair superalloy components. In several processes, the defects are cleaned using fluoride ions (U.S. Pat. No. 4,098,450) or hydrogen (J. C. Bake, *Welding J.*, Res. Supp., Aug., pp. 559-566 (1971)) to remove oxides from the crack or flaw surfaces. A braze alloy is then flowed into the gap to effect the repair or form a joint. One problem with this technique is the adequacy of the cleaning procedures. If the crack surfaces are inadequately cleaned, incomplete joints will form. The second problem is that, as with weld joints, brazed joints are typically much weaker than the base alloy. Diffusion brazing is a variation of this procedure (U.S. Pat. No. 3,678,570) in which the filler alloy has a composition similar to the base alloy and strengths approaching the base metal levels can be obtained. However, to permit reasonable joining times to be obtained, very thin joint gaps are used to obtain these strength levels. Such thin gaps are not common in repair situations.

An alternative approach for repair and joining using braze filler materials employs wide gap brazing mixtures which are mixtures of a higher melting alloy and a brazing alloy which may be of the conventional type (U.S. Pat. No. 3,155,491) or of the diffusion brazing type (U.S. Pat. Nos. 4,381,944 and 4,008,844). The higher melting alloy is typically of a composition similar to the base metal being joined, while the brazing alloy usually contains 2-4% of boron and silicon. Mixtures containing from 30-70% braze alloy have been used. An inhomogeneous structure of alloy particles in a braze alloy matrix is typically obtained. Diffusion heat treatments can be used to make the microstructure more uniform. However, the mean level of melting point depressants in the joint is still 1-3% of boron and silicon. For this type of repair, the defect is ground out prior to the use of the braze mixture, thus eliminating the problem of inadequate cleaning. However, the strength of the joint is still substantially lower than that of the base metal, limiting such repairs to low stressed areas. The use of this technique is also limited by the compatibility of the filler with the protective coatings used on turbine components. Antony & Goward, *Super-*

*alloys*, pp. 745-754 (1988). The high level of melting point depressants such as silicon and boron interfere with the performance of the coatings.

In one description of wide gap brazing, it is reported that the high melting point alloy can be sintered into the joint to form a porous structure which is infiltrated with braze alloy in a subsequent step. Chasteen & Metzger, *Welding J. Res. Supp.*, pp. 111s-117s (Apr. 1979). This results in a distinctly nonuniform structure of powder particles in a matrix of braze alloy which has mechanical properties lower than the base metal and higher than a pure braze joint.

It has been suggested that liquid phase bonding can be used to join nickel base superalloys. M. Jeandin, et al., *High Temp. Tech.*, Vol. 6, No. 1, pp. 3-8 (February 1988). In this process, conventional superalloy powders are placed in the joint, heated to a temperature where they are partially liquid and accelerated sintering occurs. Unfortunately, at these temperatures the base alloys being joined are also partially liquid making the technique unsuitable for repair or joining of finished shape parts.

The above references are hereby incorporated by reference.

### SUMMARY OF THE INVENTION

The present invention relates to methods for joining or repairing discontinuities in metallic articles.

The present invention also relates to filler compositions to be used in such a method.

### BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described with reference to the drawings which are not considered to limit the invention.

FIGS. 1(a), 1(b), 1(c), 1(d), 1(e), and 1(f) depict the progression of the repair method of the present invention;

FIGS. 2(a), 2(b), 2(c), 2(d), and 2(e) depict the progression of an alternative embodiment of the invention; FIGS. 3(a) and 3(b) show an alternative embodiment of the invention involving forming a layer over a defect;

FIG. 4 is a photomicrograph of the joint formed in Example 1(a); and

FIG. 5 shows the stress rupture properties of the joint formed in Examples 1 and 2.

### DETAILED DESCRIPTION OF THE INVENTION

The method of the present invention involves cleaning the surface of the article to be repaired or joined in the region of the joint, as shown in FIG. 1(a). A powder with desirable mechanical properties or environmental resistance is applied to the joint in the sufficient quantity to fill the void, as shown in FIG. 1(b). The whole component or fabrication is heated in a vacuum, an inert atmosphere or a reducing atmosphere to a temperature where solid state sintering of the powder can take place. The component or fabrication is held at that temperature for sufficient time to effect partial densification of the powder. Upon cooling, a porous metallic structure is obtained in the joint or repair area, as shown in FIG. 1(c). A layer of braze alloy with a composition similar to the base alloy or powder is applied to the surface of the porous region, as shown in FIG. 1(d). The braze alloy or powder composition is modified from the base alloy composition by the addition of melting point depres-

sants which lower the solidus to a temperature below the sintering temperature previously used. The component or fabrication is heated in a vacuum to a temperature which causes the braze alloy to melt. While at temperature, the braze alloy is drawn into the porous region and partially fills the interstices in the porous region (FIG. 1(e)). The presence of the liquid phase promotes sintering, resulting in the relatively complete densification of the powder in the joint region. After sufficient time to effect full densification, the component or fabrication is cooled. The result of the process is a joint which is 99+ % dense (FIG. 1(f)). The joint also contains a minimum of melting point depressants, because only enough braze alloy to promote liquid phase sintering need be used. For this reason, properties approaching those of the base metal can be obtained and compatibility with coating systems is not problematic.

In the preferred embodiment of the invention, the base metal of the articles being repaired or joined is one of the family of iron, nickel, or cobalt based superalloys. If the region to be repaired contains defects, those defects are removed by grinding or cutting the damaged area.

The surface to which the powder metal filler is to be applied are cleaned using abrasive or chemical means to expose bright unoxidized metal. Alternatively, the process can be carried out in a gaseous atmosphere which is capable of removing oxide layers. Hydrogen containing reducing atmospheres or vacuum are suitable for aluminum-free alloys while fluorine bearing atmospheres may be used for alloys containing aluminum.

The joint or void is filled with powder metal which has desirable mechanical and/or environmental resistance characteristics. In particular, the composition may be selected to have high tensile strength, creep strength, hardness, oxidation resistance, corrosion resistance or wear resistance. In some instances, powder of the same composition as the base metal may therefore be used. The powder size may be any available grade. It is preferred to use a mixture of coarse and fine particle sizes, because this results in greater initial packing density, promotes sintering, and reduces the amount of braze alloy necessary for liquid phase sintering. To assist in keeping the powder in place during handling, a binder compound which will evaporate at high temperatures may be used. Mechanical dams may also be used to prevent the powder from flowing out of the joint or void. Some overfilling of the joint is necessary to accommodate shrinkage during sintering.

The fabrication of component being repaired is placed in a furnace under an inert atmosphere, reducing atmosphere or vacuum and is heated to a temperature suitable to promote solid state sintering of the powder, typically in the range of 1000°-1400° C. The temperature must be chosen to prevent detrimental effects in the base alloy. It must be below the solidus of the base alloy to prevent incipient melting and at a low enough temperature that no solid state degradation such as grain growth or irreversible phase transformations occur. The part is held at temperature for sufficient time for partial solid state sintering to occur. Solid state sintering is the process by which particles in a powder mass or compact are consolidated by solid state and surface diffusion, wherein the powder remains solid. Partial solid state sintering results in a porous structure which is less than 100% dense. Times of 20 minutes to 24 hours are adequate depending on the temperature chosen. The parts are then cooled to ambient temperature.

A thin layer of low melting braze alloy is then added to the surface of the partially sintered region. Typically, a layer of 0.5-3 mm is added. The powder composition is selected on the same basis as the powder initially used, as described above. Additions of melting point depressants such as boron and silicon are made to lower the solidus below the sintering temperature. The minimum amounts of melting point depressants necessary to achieve this are used, typically, amounts of 0.1 to 2% Boron and 0.1 to 2% Silicon are used. The alloy may be added as a powder or in the form of a tape or foil.

After the application of the braze alloy, the component or fabrication is placed in a furnace under vacuum or in an inert or reducing atmosphere and heated to a temperature similar to that used for the partial sintering cycle, typically in the range of 800°-1600° C., preferably 1,000°-1,400° C. The temperature is selected to be such that the low melting braze will be liquid, and wet the surfaces of the pores in the previously sintered area. The component is held at temperature for a sufficient interval to promote liquid phase sintering, typically, 20 minutes to 24 hours. Liquid phase sintering is the process by which adjacent particles in a powder mass are consolidated principally by diffusion through a liquid phase present between the particles. The component or fabrication is then cooled to room temperature. The component is then given a suitable heat treatment to develop mechanical properties in the joint and the base metal. Hot isostatic pressing can be used as part of the heat treatment to close any minor internal porosity. Hot isostatic pressing is the process of simultaneously exposing the component to high pressures (10-50 KSI) and temperatures greater than 1000° C.

The result of the process is a component or fabrication with joints or repaired areas having mechanical properties similar to those of the base metal and containing a minimum of melting point depressant additions.

It is equally possible to form joints or repair areas by applying both the powdered metal and the low melting braze alloy simultaneously, either in alternate layers or as a mixture. The component is then processed by partial sintering at a temperature wherein all of the constituent alloys remain solid. The partially sintered area is then further heated to a temperature wherein the low melting braze is liquid and liquid phase sintering can take place.

In another embodiment of the invention, a partially sintered layer of powder metal is prepared by the method described above, as shown in FIG. 2a. A layer of low melting braze alloy is then applied over the surface of the partially sintered area (FIG. 2b) and the component is heated to a temperature at which melting of the braze takes place, but no significant infiltration occurs. This temperature is lower than that required for full infiltration and is typically between 800° and 1200° C. This results in the formation of a skin over the sintered layer which effectively encapsulates the partially sintered region upon cooling (FIG. 2c).

Finally, the component is subjected to a hot isostatic pressing cycle in which high gas pressures (10-50 psi) and temperature below the remelting temperature of the braze (800°-1200° C.) are employed to result in densification of the partially sintered region (FIG. 2d). The outer skin which contains material of the braze composition can then be removed (FIG. 2e). This results in a joint containing substantially no material of the braze composition.

Similarly, defects in an article may be repaired. The surfaces of the defect are cleaned by exposure to a suitable atmosphere which can remove surface oxides, for example, hydrogen or fluorine. A layer is formed over the defect, as shown in FIG. 3(a) using the two-step process of solid state sintering and liquid phase sintering described above. This layer effectively encapsulates the defect and seals it from the outer surface. The component is then given a hot isostatic pressing treatment. The pressure differential between the surface of the components and the defect surfaces causes the defect to collapse and results in diffusion bonding of the surfaces. The defect is thus eliminated from the component, as shown in FIG. 3(b).

#### EXAMPLES

The invention will now be described with reference to certain examples that are not considered to limit the invention.

##### EXAMPLE 1(a)

Joints are between plates of IN738, a nickel base alloy with a nominal composition of 16% Cr, 8.5 Co, 1.75% Mo, 2.6% W, 0.9% Nb, 3.4% Ti, 3.4% Al, 0.01% B, 1.75% Ta, Ni bal and Si as low as possible. A powder mixture of -140 mesh and -325 mesh particle sizes with a matching composition is partially sintered in the joint by exposing it for 4 hours at 1200° C. in vacuum. A layer of braze alloy with a nominal composition the same as the base alloy but with the addition of 1% B and 1% silicon is applied over the joint area. The joint is heated at 1200° C. for 4 hours in vacuum and is subsequently aged at 1120° C. for 2 hours and 845° C. for 24 hours. The processing resulted in the formation of a sound dense joint, as shown in FIG. 4. Samples removed from the joint and tested by stress rupture testing show the joint to have creep strength approaching those of the base alloy, as shown in FIG. 5.

##### EXAMPLE 1(b)

A layer of IN738 powder is deposited on the surface of an AISI 304 stainless steel sheet using the method of example 1(a). The thickness of the sheet is increased 0.025 inches by the continuous layer formed on the surface. This layer increases the oxidation resistance of a material.

##### EXAMPLE 2

In a second instance, a joint is prepared between plates of IN738 alloy using a -325 mesh powder of Rene 80 powder with a nominal composition of 14% Cr, 9.5% Co, 4% Mo, 4% W, 5% Ti, 3% Al, 0.015 B and Ni balance. The joint is partially sintered at 1200° C. in vacuum for 2 hours. A layer of braze alloy of the same composition used in the first example is placed over the joint. The joint is heated to 1200° C. for two hours in vacuum and aged at 1120° C. for two hours and 845° C. for 24 hours. The resulting joint is sound and dense. The stress rupture properties are similar to those of the base metal, as shown in FIG. 5.

##### EXAMPLE 3

Repairs of damaged turbine blades and vanes are made using the technique outlined in Example 2. In one instance,  $\frac{3}{4}$  inch cracks in a Rene 80 alloy turbine vane segment are repaired by removing the damaged area and filling it with matching alloy powder of -325 mesh. In a second instance, a Rene 80 alloy turbine

blade which had worn by rubbing at its tip has a powder buildup applied to increase its height by 0.100 inches. Both parts are processed, as in Example 2.

##### EXAMPLE 4

For a comparison, a powder buildup is prepared on an AISI 304 stainless steel substrate using the technique of Chasteen & Metzger, supra. A layer of Rene 80 powder is sintered at 1130° C. for 30 minutes. A layer of braze of composition 7% Cr, 3% Fe, 6% W, 4.5% Si, 3% B and balance nickel is deposited over the sintered layer and processed at 1130° C. for 30 minutes. The result is distinctly a two component structure consisting of alloy particles in a braze alloy matrix. This is in contrast with the result of the present invention which yields a uniform microstructure.

##### EXAMPLE 5

Joints are prepared from IN738 alloy in an identical fashion to that described in Example 1. Subsequent to the processing of Example 1, the parts are processed through a hot isostatic pressing cycle at 1200° C. and 15,000 psi argon gas pressure for 2 hours. This processing eliminated all residual porosity. Stress rupture bars are machined and tested from these joints. As shown in FIG. 5, the properties approach those of the base metal.

##### EXAMPLE 6

A welded IN738 alloy turbine blade containing welding cracks is processed to eliminate the cracks. The cracked areas are not removed prior to processing. A layer of matching alloy powder is applied over the cracked area and sintered at 1200° C. for 4 hours in vacuum. A layer of braze alloy of the same composition used in Example 1 is then applied, and the blades are processed at 1200° C. for 4 hours in vacuum and hot isostatic pressed at 1200° C. for 2 hours at 15,000 psi argon pressure. The surface deposit is removed after processing. Metallographic examination revealed that the cracks are entirely eliminated.

##### EXAMPLE 7

An IN738 alloy turbine blade tip, as in Example 3, is repaired by an alternative process in which a layer of IN738 powder is first deposited to a thickness of 0.100 inches. A second brazing alloy having a composition the same as the IN738 alloy but with the addition of 1% B and 1% Si is applied on top of the first layer. The blade is heated at 1050° C. for 4 hours under vacuum causing partial sintering of both powders. The blade is subsequently heated in the same furnace cycle to 1200° C. for 4 hours where melting of the braze alloy occurs resulting in complete liquid phase sintering of the IN738 powder. The blade is subsequently aged at 1120° C. for 2 hours and 845° C. for 24 hours. After this heat treatment, the blade tip is restored to its original shape by grinding. Sintering and brazing may thus be completed during one thermal cycle when the sintering temperature is below the solidus temperature of the brazing alloy.

##### EXAMPLE 8

An IN738 alloy turbine blade is repaired, as described in Example 7, however, a homogeneous mixture of the IN738 and braze alloy powders is placed over the damaged area. The powder mixture consists of 30% braze and 70% IN738. Using the same thermal cycle as described in Example 7, the powders sinter partially at

1050° C. by solid state, diffusion, followed by complete liquid phase sintering at 1200° C. The original blade dimensions are restored by grinding to remove excess material following heat treatment.

#### EXAMPLE 9

A crack in an IN792 turbine wheel is removed by grinding leaving a notch approximately  $\frac{1}{4}$  inch in depth and  $\frac{1}{4}$  inch wide. This notch is filled with IN738 alloy powder, such that there is an excess of this material around the joint. The IN738 powder is sintered at 1050° C. for 4 hours under vacuum. A second layer of a commercial brazing alloy (100) having a nominal wt % of 19 Cr, 10 Si—balance Ni is applied over the first sintered layer. The part is then heated to 1100° C. under vacuum for 30 minutes causing partial melting of the brazing alloy, sealing of the surface and limited infiltration of brazing alloy into the surface of the sintered powder. The first sintered layer retains its porous structure until it is further processed by hot isostatic pressing (HIP) at 1050° C. and 50,000 psi argon gas pressure for 4 hours. During this cycle, the IN738 powder is completely consolidated. The braze alloy does not melt during the final cycle and acts as an encapsulating layer for the IN738 powder during the HIP cycle. Excess braze and IN738 alloy are removed from the part by a grinding procedure.

#### EXAMPLE 10

A modification is made to an IN738 turbine blade to substantially improve the corrosion resistance of the blade tip. The blade height is first reduced 0.050 inches by grinding. A commercial alloy (995) containing 32 Ni, 21 Co, 8% Al, 0.5 Y and a balance of cobalt (commonly referred to as an M Cr Al Y alloy) is deposited to a thickness of 0.050 inches on the tip area of the blade. This layer is first heat treated at 1200° C. for 4 hours at a pressure of  $10^{-5}$  Torr, causing partial sintering of the powder. A second commercial powder (100) having 19% Cr, 10 Si with a balance of nickel is deposited on top of the first layer. This structure is heat treated at a temperature 1155° C. for 30 minutes and a pressure of  $10^{-5}$  Torr causing liquid phase sintering and complete consolidation of the first layer. The blade tip is subsequently restored to its original dimensions. The additional concentrations of Cr, Al, Si and Y in the tip deposit result in reduced rates of environmental attack as compared to the base alloy material, under similar service conditions.

#### EXAMPLE 1

The wear mechanism which occurs between the tip of a rotating IN738 turbine blade and an abradable seal material is favorably altered by introducing hard ceramic particles in a metal matrix to the tip of the blade. A mixture of ceramic particles, ranging in size from 0.001 to 0.020 inches and a nickel or cobalt base alloy powder is deposited on the tip of a turbine blade. The ceramic particles are composed of aluminum oxide. The metal alloy powder may be the same as the blade alloy or an M Cr Al Y alloy. The deposit is heat treated at 1100° C. for 4 hours at a pressure of  $10^{-5}$  Torr causing partial sintering of the metal powder which contains the ceramic particles. A second commercial powder (100) having a composition 19% Cr, 10% Si and a balance of nickel is deposited over the first layer. The articles is then heat treated at 1155° C. for 30 minutes at  $10^{-5}$  Torr causing liquid phase sintering and complete consolidation

tion of the first layer. The blade tip is then machined to the required dimensions, exposing the ceramic particles in the metal deposit. Wear between the blade tip and the shroud material now occurs by a cutting mechanism rather than an adhesive process which leaves a smooth seal surface. Under these conditions, wear of the blade tip is decreased and operational efficiency of the gas turbine is improved.

Although the invention has been described in conjunction with specific embodiments, it is evident that many alternatives and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, the invention is intended to embrace all of the alternatives and variations that fall within the spirit and scope of the appended claims.

#### We claim:

1. A method for liquid phase sintering comprising, partially solid state sintering a metallic powder onto a metallic or alloy substrate at a temperature where the metallic powder and the substrate remain solid, applying a layer of alloy having a melting point lower than that of the metallic powder and the metallic or alloy substrate to a surface of the sintered metallic powder and liquid phase sintering the sintered metallic powder with the lower melting alloy at a temperature at which the metallic or alloy substrate is solid, wherein the metallic powder, the metallic or alloy substrate, and the lower melting alloy have similar nominal compositions, with the lower melting alloy containing amounts of additional elements to reduce its melting point.

2. The method according to claim 1, wherein the metallic powder, the metallic or alloy substrate, and the lower melting alloy are selected from iron, nickel, or cobalt based superalloys.

3. The method of claim 2, wherein the superalloy comprises 8-35 wt % Cr, 0-15 wt % W, 0-15% Mo, 0-10% Ta, 0-6% Nb, 0-6% Al, 0-6% Ti, 0-5% Hf, 0-1% Y, 50-80% Ni, and/or Co, and/or Fe.

4. The method according to claim 3 wherein the partial sintering step is performed in the temperature range 800°-1600° C.

5. The method according to claim 3 wherein the partial sintering is performed in the temperature range 1000° to 1400° C. in a protective atmosphere.

6. The method of claim 3 wherein the liquid phase sintering is performed in the temperature range 800°-1600° C.

7. The method according to claim 3 wherein the liquid phase sintering is performed in the temperature range 1000° to 1400° C. in a protective atmosphere.

8. The method according to claim 3, wherein the additional elements are 0.1-2% Silicon, 0.1-2% Boron, or both.

9. A method for repairing or joining of metallic or alloy articles comprising, mechanically cleaning the repair or joint area to remove oxides and defects, applying a metallic powder to fill the repair or joint area, heating the repair or joint to effect partial solid state sintering of the metallic powder, applying a layer of alloy having a melting point lower than the metallic powder and the articles being repaired or jointed, heating the repair or joint to effect melting of the lower melting alloy, and liquid phase sintering of the metallic powder at a temperature at which the articles being repaired or joined and the metallic powder remains solid, wherein the metallic powder, the metallic or alloy article to be joined or repaired, and the lower melting alloy have similar nominal compositions, with the lower

melting alloy containing amounts of additional elements to reduce its melting point.

10. A method for liquid phase sintering comprising, first applying to a metallic or alloy substrate a mixture of a metallic powder having a melting point equal or greater than the metallic or alloy substrate and a low melting alloy powder having a melting point lower than the metallic or alloy substrate, second partially solid state sintering the powder mixture at a temperature above the melting point of the low melting alloy and liquid phase sintering the partially sintered powder mixture at a temperature above the melting point of the low melting alloy, wherein the metallic powder, the metallic or alloy substrate, and the lower melting alloy have similar nominal compositions, with the lower melting alloy containing amounts of additional elements to reduce its melting point.

11. A method of repairing or joining or adding material to metallic or alloy articles comprising; the application of a metallic powder to fill the joint or repair area, heating the joint or repair area to effect partial solid state sintering of the metallic powder, application of a layer of an alloy having a lower melting point than the metallic powder and the metallic or alloy articles, heating the joint or repair area to a temperature at which melting of the braze alloy occurs, but at which minimal flow occurs resulting in liquid phase sintering of a skin over the partially sintered region, hot isostatic pressing of the article to effect densification of the partially sintered area.

12. A method of preparing a wear resistant layer on alloy articles comprising applying a mixture of metallic powder and hard particles, heating the article to effect partial solid state sintering of the metallic powder, applying a layer of alloy having a melting point lower than the metallic powder and the alloy article, heating the article to effect melting of the low melting alloy and liquid phase sintering of the metallic powder at a temperature at which the article and the metallic powder remain solid.

13. The method according to claim 12 in which the hard particles are particles of metal nitrides, oxides, carbides, borides, or mixtures thereof.

14. A method for liquid phase sintering comprising, partially solid state sintering a metallic powder onto a metallic or alloy substrate at a temperature where the metallic powder and the substrate remain solid, applying a layer of alloy having a melting point lower than that of the metallic powder and the metallic or alloy substrate to a surface of the sintered metallic powder and liquid phase sintering the sintered metallic powder

with the lower melting alloy at a temperature at which the metallic or alloy substrate is solid, wherein the low melting alloy is of the same nominal composition as the metallic or alloy substrate with the addition of 0.1-2% Silicon, 0.1-2% Boron, or both.

15. The method according to claim 14, wherein a mixture of coarse and fine metallic powder particle sizes is used.

16. The method according to claim 14, wherein the articles are gas turbine components.

17. A method for liquid phase sintering comprising, partially solid state sintering a metallic powder onto a metallic or alloy substrate at a temperature where the metallic powder and the substrate remain solid, applying a layer of alloy having a melting point lower than that of the metallic powder and the metallic or alloy substrate to a surface of the sintered metallic powder and liquid phase sintering the sintered metallic powder with the lower melting alloy at a temperature at which the metallic or alloy substrate is solid, wherein the component is subsequently hot isostatically pressed.

18. The method of claim 17, wherein the sintered layer is formed to seal a defect in the substrate which is closed by subsequent hot isostatic pressing.

19. A method for liquid phase sintering comprising, partially solid state sintering a metallic powder onto a metallic or alloy substrate at a temperature where the metallic powder and the substrate remain solid, applying a layer of alloy having a melting point lower than that of the metallic powder and the metallic or alloy substrate to a surface of the sintered metallic powder and liquid phase sintering the sintered metallic powder with the lower melting alloy at a temperature at which the metallic or alloy substrate is solid, wherein the layers of the metallic powder and low melting alloy are applied prior to processing and the partial sintering and liquid phase sintering steps are subsequently performed in a single thermal cycle.

20. A method for liquid phase sintering comprising, partially solid state sintering a metallic powder onto a metallic or alloy substrate at a temperature where the metallic powder and the substrate remain solid, applying a layer of alloy having a melting point lower than that of the metallic powder and the metallic or alloy substrate to a surface of the sintered metallic powder and liquid phase sintering the sintered metallic powder with the lower melting alloy at a temperature at which the metallic or alloy substrate is solid, wherein the metallic powder contains 17-31% Cr, 6-11% Al, 0.5-1% Y and a balance of nickel, cobalt, or iron.

\* \* \* \* \*

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**United States Patent** [19]  
**Wertz et al.**

[11] **Patent Number:** 4,822,248  
[45] **Date of Patent:** \* Apr. 18, 1989

[54] **REBUILT SHROUDED TURBINE BLADE  
AND METHOD OF REBUILDING THE  
SAME**

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[\*] **Notice:** The portion of the term of this patent  
subsequent to Feb. 28, 2006 has been  
disclaimed.

[21] **Appl. No.:** 33,855

[22] **Filed:** Apr. 15, 1987

[51] **Int. Cl.<sup>4</sup>** ..... F01D 5/12; F01D 5/14;  
F01D 5/20

[52] **U.S. Cl.** ..... 416/192; 29/156.88;  
29/402.07; 29/402.18; 29/330

[58] **Field of Search** ..... 29/156.8 B, 156.8 R,  
29/402.06, 402.07, 402.13, 402.18, 527.5, 530;  
416/192, 224, 241 R, 213 R, 213 A, 228 R, 241  
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*Primary Examiner*—Howard N. Goldberg

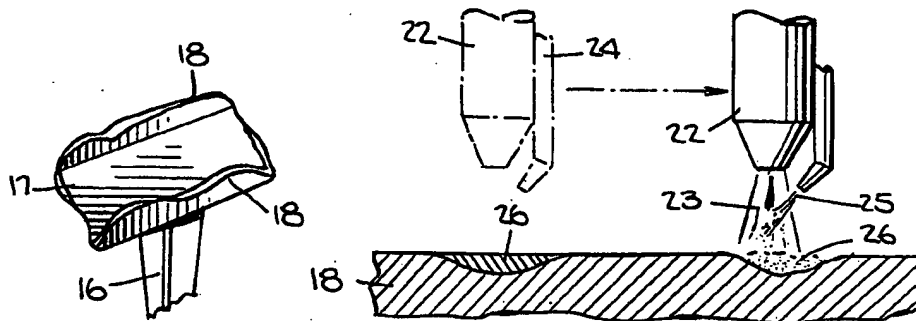
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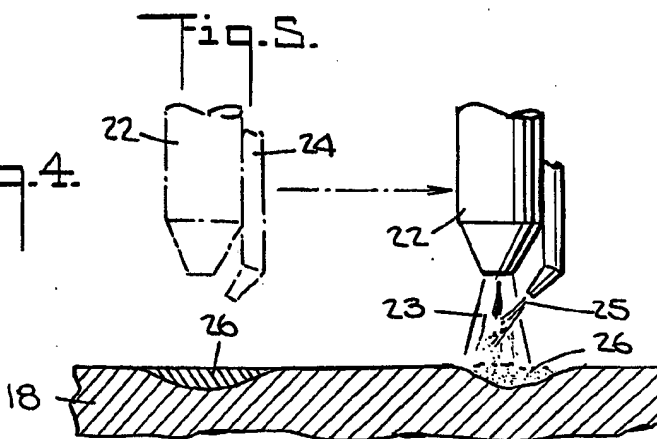
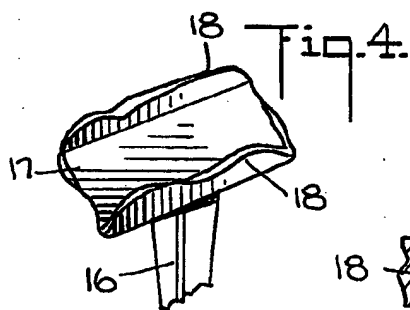
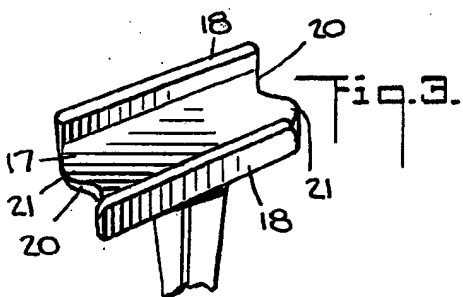
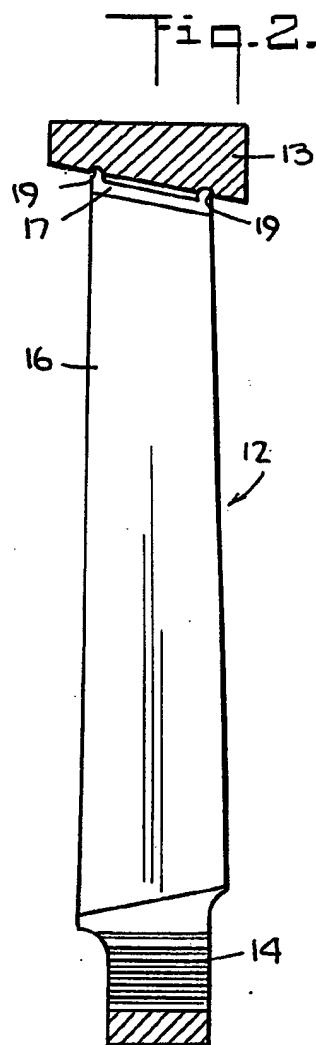
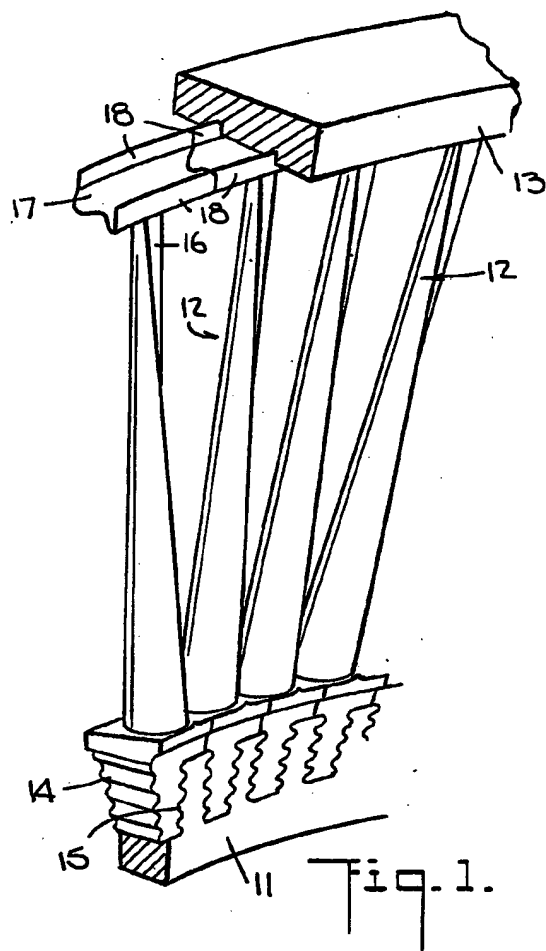
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[57] **ABSTRACT**

The shrouded turbine blade is provided with a wear resistant surface on the seals as well as along the abutment faces including the notched edges. The wear surfaces are characterized in being metallurgically bonded to the base material of the shroud without significant dilution by the base material. This is accomplished by using transparent plasma arc welding at a low amperage and a low temperature. The wear resistant surface can be of a material different from the base material of the shroud proper.

18 Claims, 1 Drawing Sheet





# REBUILT SHROUDED TURBINE BLADE AND METHOD OF REBUILDING THE SAME

This invention relates to a shrouded turbine blade. More particularly, this invention relates to rebuilt gas turbine engine blades having a design configured in what is known as a shrouded airfoil.

As is known, gas turbine engines frequently employ shrouds on airfoils, such as described in U.S. Pat. Nos. 4,589,175; 4,291,448; 4,155,152 and 4,128,929, to add mechanical stiffness and to guide a flow of air or gas over the airfoils. To this end, each airfoil is formed with an elongated curved blade with a shroud at the tip. The shroud is generally of flat shape, and may or may not have one or more upstanding ribs which project into grooves of a surrounding seal ring to act as seals. In addition, each shroud is provided on two opposite edges with abutment faces, sometimes configured as so-called Z-notches. When a series of such airfoils are mounted about a mounting ring, the ribs of the airfoils are aligned circumferentially and are disposed to move within the grooves of a surrounding seal ring. The notches, on the other hand, fit into each other so that the shrouds define a continuous annular surface.

During use, these airfoils are generally subjected to wear at the abutting surfaces of the shrouds for various reasons. Thus, over time, the airfoils require refurbishment or replacement. However, in many cases, these airfoils have simply been replaced rather than being refurbished since attempts to repair or restore the airfoils have not been successful or economical. This has been due to the fact that with conventional weld repairs high thermal stresses are usually imposed upon the airfoil tips in order to provide a rebuilt surface. This, in turn, produces weakened areas which may subject the blade to damage or total loss during subsequent use.

Generally, the airfoils and shrouds are made with rather thin cross-sections. Hence, it becomes rather difficult to form a wear resistant surface on the seal tips, abutment faces and in the Z-notches of such shrouds. Further, in those cases where the worn shrouds have been restored, relatively complex, time-consuming operations have been performed, such as described in the above-noted patents. For example, in some cases, an overlay is built up on a worn edge using welding material and then the overlay is ground down to an original size. In other cases, a built-up edge is made by plasma spraying of molten metal powder through a mask in a mold and then the edge is sintered at high temperatures to season the bond to the base metal.

Accordingly, it is an object of the invention to rebuild the worn shroud of an airfoil without the introduction of the stresses in the shroud.

It is another object of the invention to provide an airfoil with a rebuilt shroud.

It is another object of the invention to provide a relatively simple technique for forming a wear resistant surface on abutment faces and seals of a shroud.

Briefly, the invention provides a shrouded turbine engine blade having a shroud at one end with a notch and a projection at each of two opposite sides and a metallurgically bonded wear resistant overlay on at least one of the notches or projections.

The shroud may also have at least one outwardly extending rib to define a seal, for example, to cooperate with a groove in a seal ring. In this case, the rib may also

be provided with an overlay in order to restore a worn surface.

The wear resistant overlay may be formed of a metal alloy such as a nickel-base or cobalt-base composition or of such a metal alloy with abrasive particles of hard material distributed throughout so as to form a composite with the metal alloy serving as a matrix for the hard particulate dispersoid. For example, the abrasive particles may be selected from the group consisting of ceramic and refractory metal carbides, nitrides or borides. Further, these particles may range in size of from 0.001 inches to 0.030 inches.

As described in U.S. Pat. No. 4,689,463, it is difficult to obtain to a weld bead deposit on a workpiece having a relatively narrow edge. However, by employing a process as described in the patent, a wear resistant overlay can be formed not only on the shroud ribs but also on the abutment faces and the Z-notches without significant melting of the shroud or use of elaborate chilling devices.

These and other objects of the invention will become more apparent from the following detailed description taken in conjunction with the accompanying drawing wherein:

FIG. 1 illustrates a perspective view of a part of a turbine rotor assembly having a series of shrouded airfoils;

FIG. 2 illustrates a side view of one airfoil of the rotor assembly of FIG. 1;

FIG. 3 illustrates a view of a shroud prior to wear;

FIG. 4 illustrates a view similar to FIG. 3 of a worn shroud; and

FIG. 5 illustrates a partial view of a shroud being restored in accordance with the invention.

Referring to FIG. 1, the turbine rotor assembly 10 includes an inner mounting ring 11, a plurality of shrouded turbine blades 12 and an outer seal ring 13. All of these components are of conventional structure and need not be described in detail. As indicated, each turbine blade 12 has a root 14 having a conventional fir tree shape seated in a suitable groove 15 of the mounting ring 11. Each turbine blade 12 also has a curvilinear airfoil 16 and a shroud 17 at the tip of the airfoil 16.

As indicated in FIGS. 1 to 3, each shroud 17 has a flat shape and may have a pair of outwardly extending ribs which define a pair of seals 18. As indicated in FIG. 1, the seals 18 of adjacent turbine blades 12 are aligned so as to form two continuous annular rings.

As indicated in FIG. 2, the seal ring 13 is provided with a pair of grooves 19 in which the ribs 18 move during rotation of the blades 12 with the mounting ring 11. These grooves 19 may be preformed in the seal ring 13 or, as is known, the seal 18 may "cut" the grooves 19 when in use.

Referring to FIG. 3, each shroud 17 is also provided with an abutment face at each of two opposite ends which define a notch 20 as well as a projection 21 at each end. The notches 20 and projections 21 are shaped in known manner to form a Z-notch and are arranged so that the shrouds 17 of adjacent blades 12 may interfit in each other in mating relation to provide a continuous annular surface. The purpose of the shroud construction is well known and need not be further described.

During use, the shrouds 17 are subjected to wear. For example, as shown in FIG. 4, the seals 18 may become worn on the upper edges, as viewed, while the notches 20 and projections 21 become worn along the faces. Of note, the amount of wear is shown in an exaggerated

manner. In order to rebuild these worn surfaces, the techniques described in U.S. Pat. No. 4,689,463 can be utilized. To this end, a wear resistant overlay is metallurgically bonded onto the worn seals 18, notches 20 and projections 21 as required. In some cases, the worn projections 21 may be overlaid with a different material from the seals 18 and notches 20 since less wear occurs to these surfaces.

A wear resistant overlay may also be metallurgically bonded onto notches 20 of new blades to prevent wear in the first place.

By way of example, as illustrated in FIG. 5, in order to restore a seal 18 to original dimensions, a plasma torch 22 is positioned opposite the worn seal 18 in order to create a transferred plasma arc 23 between an electrode (not shown) of the torch 22 and the seal 18. In addition, a suitable powdered metal feed tube 24 is provided to feed powdered metal particles 25 into the arc 23 for depositing on the seal 18. Although the torch 22 and powdered metal feed tube 24 are shown in side-by-side relation, any other suitable arrangement may be used.

Practically speaking, rather than individual portions of a seal 18 requiring restoring, the entire tip surface of the seal normally requires some degree of restoring. To this end, the torch 20 is operated as described in the U.S. Pat. No. 4,689,463 so that a series of overlapping weld deposits is formed along the narrow surface of the seal 18. As indicated, the overlay forms a wear resistant surface 26 for example, of a width of from 0.020 to 0.250 inches and a thickness of from 0.010 to 0.120 inches, and is characterized in being metallurgically bonded to the seal proper.

For example, for an airfoil having a blade length of approximately  $4\frac{1}{2}$  inches and a shroud having a seal with a thickness of 0.025 inches and a height of 0.050 inches, the torch 22 may be operated at an amperage of from about 3 amps to 8 amps. At such low amperage, the amount of heat imparted to the seal 18 can be held to a minimum while at the same time providing sufficient heat to melt and cast the powdered metal to form an overlay metallurgically bonded to the seal proper. Conventionally, airfoils may have a blade length of from 2 inches to 24 inches.

In order to restore the notches 20 and projections 21, the turbine blade 12 can be mounted in a suitable workholder and manipulated relative to a torch or vice versa or both the torch and the work may be manipulated in a coordinated motion so that a similar wear resistant overlay can be formed. Generally, the flat portion of the shroud is thicker than the seals, for example having a thickness of about 0.030 inches to 0.100 inches. Thus, application of the overlay to the notches and projections can be performed at a somewhat higher amperage, for example in the range of from 5 to 15 amps. In the event that excessive heat might be transferred to the shroud 17, the arc circuit may be pulsed, for example, as described in U.S. Pat. No. 4,689,463 so as to reduce the amount of heat generated.

In order to achieve greater thicknesses of wear surface, such as where the amount of wear is not uniform, multiple passes of the torch may be made on the shroud surfaces.

In some cases, it may be necessary to lay down excess material in a notch or on a projection of a shroud. In such cases, the amount of excess material is less than that applied in conventional weld repair. This excess material may be subsequently ground out and the

shroud thereafter polished to provide accurate surfaces for mating when mounted in place.

The material used for the overlay may be any suitable powdered metal material compatible with the material of the shroud. For example, a cobalt-base material having a composition of 30% Cr, 20% W, 5% Ni, 1% V, 0.85% C, and the balance Co, may be used. Other nickel-base or cobalt-base materials or an alloy of such materials with abrasive particles of a hard material distributed therein may be used.

The invention thus provides the shroud of a blade with a surface which is metallurgically bonded on the seals, projections and/or notches, which is wear-resistant and which is highly resistant to spalling or chipping.

Further, the invention provides a restored shrouded airfoil having a structure substantially equivalent to that of an originally manufactured blade. Thus, instead of scrapping blades having worn shrouds, the shrouds can be rebuilt and the blades returned for use.

The invention also provides a means for providing a wear resistant surface which can be metallurgically bonded to the notches of new turbine blades.

The wear resistant overlays which are formed on the shroud can be characterized in that each forms a hard wear resistant surface metallurgically bonded to the shroud proper.

Further, the amount of dilution of the overlay by the base material of the shroud is held to a minimum so that the applied material of the wear surface can be a different material from the base material of the shroud.

Further, the wear surfaces can be distinguished in that relatively low heat is required in order to metallurgically bond the wear resistant overlay to the base material of the shroud proper. Still further, the wear surfaces can be distinguished from plasma sprayed coatings which are mechanically bonded as applied, in that the wear surfaces provided by the invention require no subsequent sintering operation and they are much more resistant to spalling and chipping in service.

What is claimed is:

1. A shrouded turbine engine blade comprising a blade root; an airfoil extending from said blade root; a shroud on said airfoil opposite said blade root, said shroud having a notch at each of two opposite ends and a projection on said opposite ends; and a metallurgically bonded wear resistant surface made from powdered metal and applied on at least one of said notches and said projections by a plasma transferred arc generated at a low amperage sufficient to melt and cast the powdered metal while holding the heat imparted to said shroud to a minimum and holding the dilution of the wear resistant surface by the base material of said shroud to a minimum.
2. A turbine blade as set forth in claim 1 wherein each wear resistant surface is of a thickness in the range of from 0.010 to 0.120 inches.
3. A turbine blade as set forth in claim 2 wherein each wear resistant surface is of a width of from 0.020 to 0.250 inches.
4. A turbine blade as set forth in claim 1 wherein each wear surface is formed of a nickel-base or cobalt base material, or of such an alloy with abrasive particles of a hard material distributed throughout.
5. A restored turbine engine blade comprising a blade root; a curved airfoil extending from said blade root;

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- a shroud on said airfoil at a distal end, said shroud having at least one outwardly extending rib to define a seal, and an abutment face at each of two opposite ends defining a notch and a projection at each of said opposite ends; and
- a metallurgically bonded wear resistant overlay made from powdered metal and applied on at least one of said rib, said notches and said projections by a plasma transferred arc generated at an amperage of from 3 to 15 amps.
6. A restored turbine blade as set forth in claim 5 wherein said overlay is of a thickness of from 0.010 inches to 0.120 inches.
7. A restored turbine blade as set forth in claim 5 wherein said airfoil and said shroud are made of a nickel-base alloy and said overlay is characterized in being a cast metal alloy.
8. A restored turbine blade as set forth in claim 5 wherein said overlay is characterized in being highly resistant to spalling and chipping and in having a minimum of dilution with said alloy of said shroud.
9. A restored turbine blade as set forth in claim 5 wherein said overlay is made of a nickel-base alloy.
10. A restored turbine blade as set forth in claim 5 wherein said overlay is made of a material different from said shroud.
11. A restored turbine blade as set forth in claim 10 wherein said overlay is made of a cobalt-base material.
12. A restored turbine blade as set forth in claim 5 wherein said airfoil and said shroud are made of cobalt-base alloy and said overlay is characterized in being a cast metal alloy.
13. A method of rebuilding a shroud of an airfoil having at least one outwardly extending rib defining a seal, said method comprising the steps of creating a transferred plasma arc between an electrode and the rib; and

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- feeding powdered metal particles into the arc for depositing a series of overlapping weld deposits on the rib to form a wear resistant layer thereon, said layer being metallurgically bonded to the rib and maintaining the transferred plasma arc at a low amperage sufficient to melt and cast the powdered metal while holding the heat imparted to the rib to a minimum and holding the dilution of the wear resistant layer by the base material of the rib to a minimum.
14. A method as set forth in claim 13 wherein the arc is generated at an amperage of from about 3 amps to 8 amps.
15. A method as set forth in claim 13 wherein the wear resistant layer is of a thickness of from 0.010 to 0.120 inches.
16. A method of rebuilding a shroud of an air foil having at least one notch thereon, said method comprising the steps of creating a transferred plasma arc between an electrode and the notch; and feeding powdered metal particles into the arc for depositing a series of overlapping weld deposits on the notch to form a wear resistant layer thereon, said layer being metallurgically bonded to the notch and maintaining the transferred plasma arc at a low amperage sufficient to melt and cast the powdered metal while holding the heat imparted to the rib to a minimum and holding the dilution of the wear resistant layer by the base material of the notch to a minimum.
17. A method as set forth in claim 16 wherein the arc is generated at an amperage of from 5 amps to 15 amps.
18. A method as set forth in claim 16 wherein the wear resistant layer is of a thickness of from 0.010 to 0.120 inches.

\* \* \* \* \*

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 4,822,248

DATED : April 18, 1989

INVENTOR(S) : TIMOTHY A. WERTZ

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 4, line 44 "form" should be -from-  
Column 6, line 29 "dilutoin" should be -dilution-

Signed and Sealed this  
Sixth Day of March, 1990

*Attest:*

JEFFREY M. SAMUELS

*Attesting Officer*

*Acting Commissioner of Patents and Trademarks*



US005211776A

**United States Patent** [19][11] **Patent Number:** **5,211,776****Weiman**[45] **Date of Patent:** **May 18, 1993****[54] FABRICATION OF METAL AND CERAMIC MATRIX COMPOSITES****[75] Inventor:** Sam M. Weiman, Cypress, Calif.**[73] Assignee:** General Dynamics Corp., Air Defense Systems Division, Pomona, Calif.**[21] Appl. No.:** 380,575**[22] Filed:** Jul. 17, 1989**[51] Int. Cl.:** B05D 1/10; B05D 1/34**[52] U.S. Cl.:** 148/525; 148/537; 427/456**[58] Field of Search:** 148/11.5 Q, 2, 3, 525, 148/537; 164/46; 427/34; 29/527.5; 428/614**[56] References Cited****U.S. PATENT DOCUMENTS**

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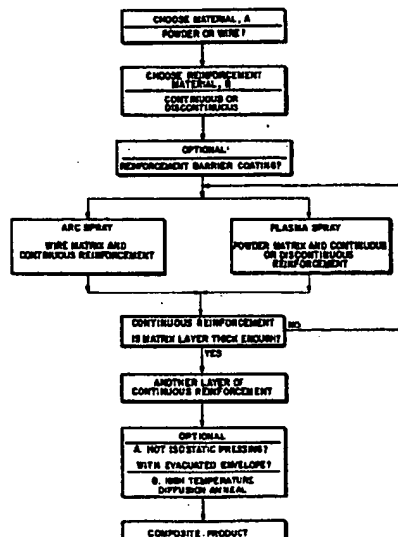
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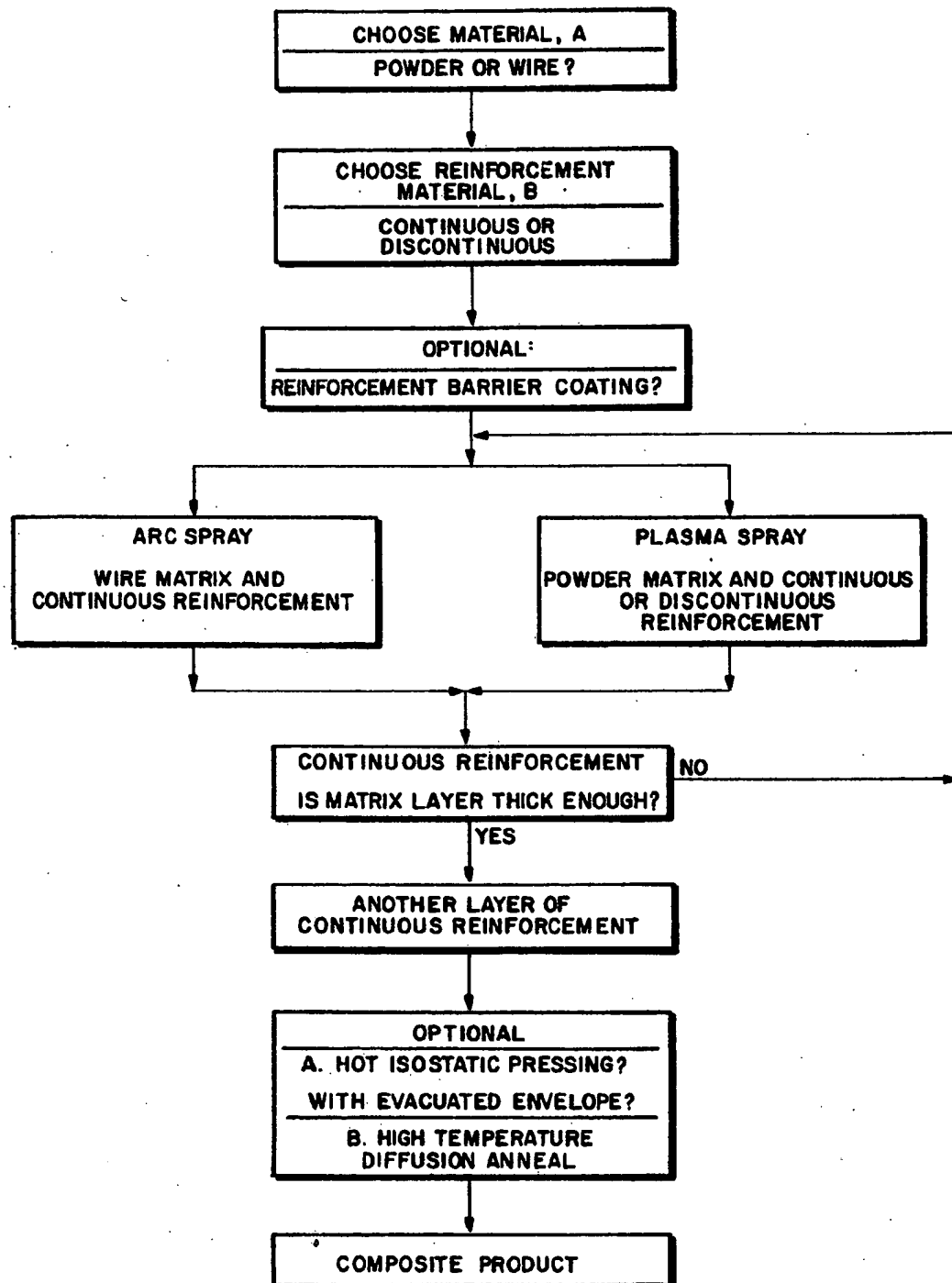
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**Primary Examiner**—George Wyszomierski  
**Attorney, Agent, or Firm**—Leo R. Carroll; Henry Bissell

**[57] ABSTRACT**

A process for manufacturing metal and ceramic matrix composite materials. The invention also encompasses various composite products made by the disclosed method. The resulting composite material comprises a reinforcement material in either continuous or discrete form embedded in a matrix material which is either a pure metal, a metal alloy, or a ceramic. The reinforcing material is optionally coated with a barrier coating material. An electric arc or plasma arc is used to spray a thin layer of matrix material over a preplaced layer of reinforcement material. Successive layers are built up until a desired object shape and thickness are achieved. There is an optional final step of high-temperature diffusion annealing or hot isostatic pressing.

**28 Claims, 1 Drawing Sheet**



## FABRICATION OF METAL AND CERAMIC MATRIX COMPOSITES

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to methods of manufacturing metal and ceramic matrix composite materials and, more particularly, to methods of manufacturing metal and ceramic composites utilizing thermal spray techniques and an optional finishing step of diffusion annealing and/or hot isostatic pressing.

#### 2. Description of the Related Art

Components for the aircraft and aerospace industries require materials having maximum specific strength and specific modulus. Specific strength is the ratio of tensile strength to density, and specific modulus is the ratio of modulus of elasticity to density. These quantities present the structural properties in terms of what used to be called the strength-to-weight ratio.

Composite structures offer significant weight economy to the engineer when used in structural designs. A composite structure consists of a continuous-phase matrix material which is made stronger and/or stiffer by a second material having a substantially higher tensile strength and/or modulus of elasticity. The material used for reinforcing the matrix can be in the form of fibers, woven textiles, or particles.

A simplified version of the theory behind the reinforcement effect of adding the high-strength/stiffness second-phase material is that the major portion of an applied load is borne by the second-phase material, while the matrix material serves to maintain the geometric and alignment relationships of individual second-phase reinforcing material elements with respect to each other for the case of continuous reinforcement. The matrix provides some degree of ductility and toughness to the composite body by transferring and distributing strain in local areas of the continuous reinforcing phase more widely to other second-phase elements and generally acts as a "glue" to hold the composite assembly together as well as to provide a feasible method of manufacturing a specific shape. The direct utilization of the reinforcing phase as a monolithic body is generally not possible because of extreme brittleness or because of difficulty or expense in obtaining it as a monolithic body. The desired strength/stiffness property of the reinforcing phase is only found in the form of structural units having very small dimensions, generally less than 0.010 inch in the smallest dimension.

In another composite form, the reinforcing phase material may be present in discrete form such as relatively short fibers of glass or silicon carbide whiskers, or short lengths of glass, carbon, graphite, partially crystallized carbon, boron or silicon carbide. These composites depend for their strength upon a degree of particle hardening. Such materials include "cermets," which are a mixture of metal and ceramic substances generally compounded with the object of producing a combination of hardness and toughness such as would be required in a tool material. Another related group of composite materials relies upon dispersion hardening, in which the movement of microscopic dislocations is impeded by strong particles having microscopic dimensions also.

If a composite material contains discrete reinforcing elements, these suffer elastic strains when the material is stressed. These elements contribute in this way to the

load-carrying capacity of the material and provide obstacles to the movement of dislocations, assuming that the elements themselves are strong. If the volume fraction of such strong elements in the composite is proportionately large, they will provide a high strength and a corresponding high load carrying capacity. One of the best ways of increasing tensile strength is by using elements in the form of long continuous fibers. The matrix material may begin to flow when stressed but in doing so will cause a force to be set up at the surface of the fiber. If the fiber is sufficiently long, the transmitted force will finally lead to its fracture and the fiber will have fully contributed to the strength of the composite material. Obviously the strength will have a maximum value parallel to the direction of the fibers.

The nature of the interface between the discrete elements and the matrix influences the extent to which the load is transferred from the matrix to the reinforcing material. Cohesion at the interface may be achieved by one of several methods:

- (1) Mechanical bonding; this involves a large enough coefficient of friction acting between the surfaces.
- (2) Physical bonding, which depends upon van der Waals forces acting between surface molecules.
- (3) Chemical reaction bonding at the interface; this, however, may give rise to weak, brittle compounds in some cases.
- (4) Bonds formed by solid-solution and diffusion effects.

Organic thermoplastic and thermosetting resin matrix composites have been in use for a long time and their fabrication methods are fully described in the technical literature. Structural metal matrix composites are relatively new and thus far only aluminum and, to a lesser extent, magnesium and copper have achieved reasonable degrees of development. Composites of these metals are obtained through powder metallurgy, liquid metal infiltration, and the diffusion bonding of alternate layers of metal foils and filaments. Ceramic matrix composites are most commonly fabricated by cold press and sinter, cast and sinter, or hot press techniques. All of the above fabrication methods suffer in varying degrees from one or more of the following problems: the presence of internal defects such as voids and incomplete diffusion bonds; the breakup of continuous filaments due to the measurable deformation of the matrix in pressing type operations; excessive reaction between the matrix and the reinforcing phase material; low bond strength between the matrix and the reinforcing phase; and very high cost.

Some examples of the art related to the fabrication of composite materials are given below.

U.S. Pat. No. 3,615,277 to Kreider et al is directed to a process of fabricating a multilayer fiber-reinforced metal matrix composite by winding a filament on a spring-loaded mandrel covered with brazing foil, preheating the mandrel, plasma arc spraying metal matrix material in coalescent form onto the filament windings so as to form a monolayer tape, and low-pressure braze bonding a plurality of tapes together in layers.

U.S. Pat. No. 3,741,796 to Walker is directed to the use of a plurality of torch flames, each resulting from the combustion of gaseous silicon tetrachloride and a mixture of hydrogen and oxygen directed upon a graphite mandrel to form a high-purity silica article upon the mandrel.

U.S. Pat. No. 3,840,350 to Tucker, Jr., is directed to a filament-reinforced composite metallic material which can be fabricated into various size filament-reinforced composite sheets or strips. A process is disclosed in which the metallic matrix of the composite consists of at least two plasma-sprayed particulated discrete metallic components which when subjected to a pressurized heat treatment will react to form a substantially homogeneous alloy matrix for the filaments.

U.S. Pat. No. 3,888,661 to Levitt et al is directed to the preparation of a graphite fiber reinforced, metal matrix composite by hot-pressing. The composite comprises layers of a matrix metal selected from the group consisting of magnesium and magnesium based alloys in combination with alternate layers of a graphite fiber. Small additions of a metal selected from the group consisting of titanium, chromium, nickel, zirconium, hafnium, and silicon are made in order to promote wetting and bonding between the graphite fibers and the matrix metal.

U.S. Pat. No. 4,141,802 to Duparque et al is directed to an improvement in fabricating composite panels comprising a metal support foil to which a fiber-reinforced metal matrix layer adheres. The improvement is to interpose a thin layer of a bonding metal or alloy between the support foil and the fiber-reinforced metal matrix layer. The bonding metal layer serves to improve the adhesion of the metal matrix to the support foil and enables the metal matrix layer to be produced under less severe conditions.

U.S. Pat. No. 4,265,982 to McCreary et al is directed to a process of coating woven materials with metals or with pyrolytic carbon by chemical vapor deposition reactions using a fluidized bed. The porosity of the woven material is retained and the tiny filaments which make up the strands which are woven (including inner as well as outer filaments) are substantially uniformly coated.

U.S. Pat. No. 4,447,466 to Jackson et al is directed to a method of fabricating gas turbine engine, superalloy airfoils and other components by a method which uses low-pressure/high-velocity plasma spray-casting and segmented mandrels.

U.S. Pat. No. 4,594,106 to Tanaka et al is directed to flame spraying compositions exhibiting improved adherence to a variety of substrates, as well as articles coated with such compositions. The spraying compositions comprise a granulated mixture of two components: (1) a powdery material selected from the group consisting of powdered metals, heat resistant ceramics, cermets, and resins; and (2) a ceramic needle fiber such as whisker crystals of SiC or Si<sub>3</sub>N<sub>4</sub>. Articles coated with thin films of these coatings exhibit thermal and corrosion resistance.

U.S. Pat. No. 4,595,637 to Eaton et al is directed to a process for plasma spraying small metal fibers onto the surface of a workpiece, and articles made using the process. An improved ceramic-faced metal article is made by spraying fibers onto the workpiece by injecting fibers into the plasma stream external to a plasma gun nozzle. Then, plasma sprayed ceramic particles are caused to surround the fibers as a matrix. Optionally a removable polymer material is interposed on the workpiece surface after the fibers are sprayed but before the ceramic matrix is sprayed to provide a low stiffness connector between a low thermal expansion coefficient ceramic material and a high expansion coefficient metal

substrate. The connector alleviates strains from thermal expansion differences.

U.S. Pat. No. 4,627,896 to Nazmy et al is directed to a method of applying a corrosion protection layer to the base of a gas turbine blade by embedding particles of SiC in a metallic matrix by means of powder, paste or electrolytic/electrophoretic methods and compacting, welding, or fusing and bonding the matrix-forming material to the base by means of hot pressing, hot isostatic pressing or laser beam, electron beam, or electric arc.

None of the patents described briefly above discloses a method of manufacturing metal and ceramic composite materials utilizing thermal spray techniques which may include the formation of in-situ alloys and wherein the method may employ multiple torches, and which is applicable to continuous fiber type reinforcement structures as well as to discrete reinforcement materials which may be sprayed, including an optional finishing step of diffusion annealing and/or hot isostatic pressing.

The current trend in the technology of warfare is toward smarter, faster, and more maneuverable tactical guided missiles. A faster, more maneuverable tactical missile results in a combination of increased loads and heating on body structures and aerodynamic surfaces. The heating problem becomes increasingly severe as the missile velocity increases beyond Mach 6. The combination of increased loads and heating exacerbates an already difficult design problem, since most structural materials demonstrate decreasing strength and stiffness with increasing temperature. For example, Rene 41 is a commonly used high-strength high-temperature nickel base superalloy. Its specific strength and specific modulus at room temperature are  $60 \times 10^4$  inches and  $1.1 \times 10^8$  inches, respectively. Values for these properties drop to  $40 \times 10^4$  inches and  $0.7 \times 10^8$  inches at 1500 degrees F. for specific strength and specific modulus, respectively, and sharply accelerate downward with increasingly higher temperatures. Current materials are also deficient in one or more of the following attributes: cost, reliability, availability, and fabricability. There is a need for new fabrication methods which will produce metal and ceramic composite materials having greater specific strength and specific modulus at high temperatures and which can be manufactured at reasonable cost. Such composites should be substantially free of matrix-reinforcement interaction and degradation.

#### SUMMARY OF THE INVENTION

In brief, the present invention involves a process for manufacturing metal and ceramic matrix composite materials. The invention also encompasses various composite products made by the disclosed method. The resulting composite material comprises a reinforcement material in either continuous or discrete form embedded in a matrix material which is either a pure metal, a metal alloy, or a ceramic or ceramic alloy. To reduce or prevent reaction between the matrix material and the reinforcement material, a barrier coating optionally can be applied to the reinforcement material prior to or during the composite fabrication process.

Although the described method is generally applicable to other metal and ceramic matrices utilizing other reinforcement phases, barrier coatings, and various matrix material feed techniques, for illustrative purposes the method is described in terms of fabricating a composite comprising a titanium matrix with continuous filament reinforcement materials. The method basi-

cally consists of using an electric arc or plasma arc to spray a thin layer of titanium or titanium alloy over a preplaced layer of reinforcement material. The reinforcement material comprises a unidirectional or bidirectional woven cloth as the strengthening/stiffening phase of the composite. Alternate metal-filament layers are built up until a desired object shape, thickness, and filament orientation are achieved.

Electric arc spraying is used for wire feeding, or plasma arc spraying for powder feeding, of titanium stock. A finishing step of a high-temperature diffusion anneal or hot isostatic pressing is desirable but not mandatory. The optional finishing step ensures that the resulting composite is homogeneous, well bonded, and free from the effects of internal voids. The finishing step is best accomplished with the composite in a "local" vacuum that is achieved by placing the composite inside an evacuated metal can or skin envelope. Since titanium is a reactive metal at elevated temperatures and could react with the reinforcing phase during the diffusion anneal or hot isostatic pressing step, if not in the spraying step, a diffusion barrier may optionally be required. This optional barrier is accomplished by coating the reinforcement material with a refractory metal such as Mo, W, or Ta or other relatively inert metals such as Co, Ni, Cu, Ag, Pd or Au or a stable oxide such as  $Y_2O_3$ ,  $Al_2O_3$  or  $TiO_2$  or a common titanium alloying element such as Al. Application of a metallic coating to the filaments is best performed by vapor deposition or electrolytic plating methods. Oxide coatings are best applied by sputtering or plasma arc spraying. For a titanium matrix and graphite reinforcement, vapor-deposited aluminum is a preferred, but not the only suitable, barrier coating. The optimum thickness of the barrier coating will be a function of the diffusion or reaction rate, which in turn depends on the coating material and the time and temperature of exposure at the elevated temperature.

#### BRIEF DESCRIPTION OF THE DRAWING

A better understanding of the present invention may be realized from a consideration of the following detailed description, taken in conjunction with the accompanying drawing in which:

The sole FIGURE is a simplified schematic flow diagram of a process for fabricating metal and ceramic matrix composite materials.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention a process is provided for manufacturing metal and ceramic matrix composite materials which encompasses a wide variety of resulting composites. The accompanying drawing figure is a simplified flow diagram of the process of the present invention. As indicated in the FIGURE, the resulting composite material comprises a reinforcement material B in either continuous or discrete form embedded in a matrix material A which is either a pure metal, a metal alloy, or a ceramic. To reduce or prevent reaction between matrix material A and reinforcement material B, an optional step in the process comprises applying a barrier coating to the reinforcement material B.

Suitable reinforcement materials in continuous filament form include graphite, silicon carbide, alumina, boron carbide, and silicon nitride. The reinforcement material B can take the form of a woven fabric. If the matrix material is a metal which is reactive at elevated

temperatures and would react with the reinforcing phase to form a weak or brittle compound during the process, a diffusion barrier must be provided. This is best accomplished by coating the reinforcement material with a refractory metal, a relatively inert metal or alloy, a stable oxide, or an element that commonly alloys with the matrix material. Possible refractory metals include the following elements and their alloys: V, Cr, Zr, Nb, Mo, Rh, Hf, Ta, W, Re, Os, Th, and Ir. The precious metals Pd, Ag, Au, and Pt, as well as Co, Ni, Cu, Sn, and Al, are also possible candidates for a barrier coating material. Stable oxides include titanium oxide, aluminum oxide and Yttrium oxide.

The application of a metallic barrier coating to a filament-type reinforcement material is best performed by vapor deposition or electrolytic plating methods. In the case of oxide barrier coatings, the best methods are sputtering or plasma arc spraying. An optimum thickness of barrier coating is a function of the diffusion or reaction rate which in turn depends on the coating material as well as the anticipated time and temperature of exposure during the manufacturing process. A desirable barrier material is one which at least wets both reinforcement and matrix materials. The ideal situation is one in which there is intimate contact between the matrix and reinforcement materials but not formation of a compound that would give rise to a zone of brittleness or weakness.

Alternatively, the reinforcement material B can take the form of discontinuous segments such as short fibers, small particles, and the like. Applying a barrier coating in the case of discrete particle reinforcement may be accomplished using a fluidized bed process or by dipping into molten metal.

The initial step in the composite fabrication process is to form a thin layer of composite material by arc spraying reinforcement material B, or barrier-coated reinforcement material B, with matrix material A. The fabrication process then basically consists of building up successive thicknesses of matrix-sprayed reinforcement layers. If the reinforcement material comprises a unidirectional or bidirectional woven cloth as the strengthening/stiffening phase of the composite, the orientation of successive layers of the fabric can be varied to give a more nearly isotropic strength and/or stiffness to the resulting composite. Thus, for example, if successive layers are oriented at 90 degrees with respect to each other, the resulting composite will be equally strong/stiff in four directions equally spaced from each other. If successive layers are oriented 60 degrees apart, the composite will be equally strong/stiff in six different directions equally spaced from each other. A successive difference of 45 degrees in angular orientation results in a composite which is equally strong/stiff in eight different directions, and so on.

There is a wide variety of materials which can be used as the matrix material. Suitable metallic matrix materials include aluminum, titanium, nickel, niobium, and their alloys. The matrix material can be applied in either wire or powder form. Suitable ceramic materials in the form of fine powder can be chosen from the group consisting of alumina, silicon carbide, boron carbide, and silicon nitride. Metallic matrix materials can be applied in wire form as either pure metals and/or prealloyed metals. If the metallic matrix material is in the form of powder, the powder can be a pure metal, an alloy, or a mixture of pure metal powders.

Thermal spraying techniques are known in the art of welding and brazing. A description of various techniques can be found in Volume 6 entitled "Welding, Brazing, and Soldering" of the *Metals Handbook*, Ninth Edition, American Society for Metals, Metals Park, Ohio 44073, published in 1983. In particular the articles on gas metal-arc welding (MIG welding), plasma arc welding, and hard facing by arc welding will be found informative in relation to the present application.

For matrix materials comprising powdered metals and ceramics, plasma arc spraying is the preferred technique. Plasma arc spraying is an arc process in which heat is produced by a constricted arc between a non-consumable tungsten electrode and a workpiece (transferred arc) or between a non-consumable tungsten electrode and a constricting orifice (non-transferred arc). When an arc is established through a gaseous column separating two electrodes, some of the gas becomes ionized into a plasma which consists of free electrons, positive ions, and neutral atoms. This current-conducting plasma part of the arc is maintained hot by the resistance heating effect of the current passing through it. Thermal ionization, which takes place in a high-temperature atmosphere, is the result of collisions of molecules and electrons in the gas and from radiation. Plasma arc welding is closely akin to gas tungsten-arc welding. Plasma is present in all arcs, and if a constriction containing an orifice is placed around the arc, the amount of plasma is greatly increased, resulting in a higher arc temperature, a more concentrated heat pattern, and higher arc voltage than can be obtained with a non-constrictive arc. In plasma arc welding two separate streams of gas are supplied to the torch. One stream surrounds the electrode within the orifice body and passes through the orifice, constricting the arc to produce a jet of very hot and fast moving plasma. This gas must be inert and is usually argon. The other stream of gas, the shielding gas, passes between the orifice body and the outer shield cup; it prevents the molten weld metal and the arc from being contaminated by the surrounding atmosphere. An inert gas or a non-oxidizing gas mixture can be used for shielding.

If the matrix material is a metal in wire form, gas metal-arc (MIG) spraying techniques are suitable. Gas metal-arc welding (often called MIG welding) is an arc welding process in which the heat is generated by an arc between a consumable electrode and the work metal. The electrode is a bare solid wire that is continuously fed to the weld area, becoming the filler material as it is consumed. The welding area is protected from atmospheric contamination by a gaseous shield provided by a stream of gas or mixture of gases fed through the electrode holder. In a spray arc, the metal is transferred from the end of the electrode wire in an axial stream of fine droplets. These small droplets come from the tapered end of the electrode. One droplet follows another but they are not connected. The spray-arc mode of transfer gives high heat input, maximum penetration, and a high deposition rate.

If the reinforcement phase comprises discrete particles, the discrete particles can be introduced in the composite fabrication process by feeding the particles in the same torch as the matrix material powder or from a second, independent torch. The initial layer of composite material is fabricated by establishing the initial layer of discrete-particle reinforcement on some sort of form. The surface on which the discrete particles are placed should be one to which they will not subsequently stick.

Alternatively, a separating compound can be applied to the surface on which the discrete particles are placed initially.

Fabrication of alloy matrices is readily accomplished by arc spraying. The desired alloy composition may be readily achieved by one of the following methods: in the form of powder either premixed in elemental form or independently fed to the same torch as prealloyed powder or as alloy powder from a second torch, or in the form of the desired alloy composition wire or as elemental or alloy wire from a second torch. When large alloy additions to the base metal are required, say greater than ten weight percent, the use of multiple independently controlled torches may be convenient. Each torch can be independently fed wire or powder as desired. It is preferable that the composite surface "aim point" for the multiple torches be identical, but this is not mandatory. The identical aim point gives greater assurance of intimate, uniform mixing of the components. The use of multiple torches is also economical because of the proportionately larger volume of material that can be applied per unit time. The economic benefits of multiple torches can be extended to volume production by using multiple sets of torches in tandem, or parallel, to fabricate large-area parts, or by utilizing multiple sets of torches to simultaneously fabricate multiples of small- and medium-area parts.

By appropriate torch and/or workpiece movement and control, associated tooling, and matching reinforcement layer shape, almost any solid part of regular or irregular shape can be fabricated. It is possible by the judicious use of permanent or removable cores to build parts with intentional internal void shapes. When separate torches or multiple feeds to a single torch are used to introduce a pure metal and an alloy, it is also possible to vary the composition of the deposited alloy to obtain tailored properties in specified locations of the part. For example, one alloy composition may be utilized for the "inside" of the part and another alloy utilized to form the "surface" of the part to provide enhanced corrosion, wear, lubrication, oxidation, etc. characteristics to the surface. Obviously the "surface" and "inside" alloys must be compatible with each other.

For metals which react with air at elevated temperatures, the deposited surface should be deposited below the reaction temperature, protected by trailing inert helium or argon gas shields, or fabricated in an inert-gas (helium or argon) or vacuum chamber. If a vacuum chamber is used, it must of course be constantly pumped.

As indicated in the drawing figure, the fabrication process of the present invention includes an optional final step of subjecting the composite product formed by previous steps to a high-temperature diffusion annealing or to a hot isostatic pressing. The purpose of this optional finishing step is to ensure that the resulting composite is homogeneous, well bonded, and free from the effects of internal voids. An isostatic hot pressing method is described in *Ceramic Bulletin*, Vol. 54, No. 2 (1975) in an article by K. H. Hardt entitled "Gas Isostatic Hot Pressing Without Molds." Isostatic hot pressing uses a gas, usually inert, to densify an object having "closed porosity" through a high isostatic gas pressure. As compared with hot pressing processes previously used, isostatic hot pressing appears to be suitable for mass production since no mold is used and the hot pressing of bodies of arbitrary shape is possible. There are no problems connected with contact between the body

being pressed and a mold or die. To minimize voids and porosity, the composite body can be isostatically hot pressed in an evacuated thin metal can or skin envelope.

In the case of metal matrices, the optional hot isostatic pressing step in the fabrication process must be tailored to the individual metal. For aluminum and its alloys, a temperature range of 900 degrees F. to 1200 degrees F. is suitable, with one to four hours being a reasonable range of pressing times. Titanium or nickel and their alloys can be hot pressed for one-quarter to four hours in the temperature range of 1700 degrees F. to 2000 degrees F. The metal niobium and its alloys are preferably pressed for one-quarter to four hours at a temperature in the range from 2000 degrees F. to 2400 degrees F.

Composite materials with ceramic matrices require somewhat higher pressing temperatures. For alumina, one hour of pressing at a temperature in the range 2800 degrees F. to 3200 degrees F. is recommended. The ceramic silicon carbide can be suitably hot pressed at a temperature in the range from 3000 degrees F. to 3400 degrees F. for a time of one hour. Boron carbide requires a temperature in the range from 3800 degrees F. to 4200 degrees F. and should be pressed for a time ranging from one to four hours. Suitable pressures for hot isostatic pressing are in the range from 10,000 to 20,000 psi. An operating gas atmosphere of helium, argon, or other non-reactive gas should be used.

As an example of a particularly attractive composition material, the case of titanium matrix composites will be briefly considered. For these matrices and a reinforcement material from the group consisting of graphite, SiC, Al<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C, and Si<sub>3</sub>N<sub>4</sub>, the metal aluminum is suitable as a barrier coating material. Aluminum is a common titanium alloying element. The application of the metallic barrier coating to the reinforcement material, say woven filament fabric, is preferably carried out by vapor deposition methods or by arc spraying. The optimum thickness of the barrier coating will depend on the anticipated time and temperature of exposure of elevated temperatures of the titanium-matrix composite material.

Although there have been shown and described hereinabove specific arrangements of a process for manufacturing metal and ceramic matrix composite materials and the products thereof in accordance with the invention for the purpose of illustrating the manner in which the invention may be used to advantage, it will be appreciated that the invention is not limited thereto. For example, besides the particular metal matrix composites which have been discussed above, others can also be fabricated by the same general process. Other metals include common structural metals and their alloys: Mg, Al, Fe, Co, Ni, Cu, Zn, Sn, and Pb; refractory metals and alloys of V, Cr, Zr, Nb, Mo, Rh, Hf, Ta, W, Re, Os, Th, and Ir; and the precious metals Pd, Ag, Au, and Pt. Particulate and continuous filament reinforcement materials could typically include B, B<sub>4</sub>C, SiC, Si<sub>3</sub>N<sub>4</sub>, BN, C, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> as well as high-strength wire such as CRES 301, Mo, Ta, and W. Attractive ceramic matrices may include, but are not limited to, Al<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C, SiO<sub>2</sub>, SiC, Si<sub>3</sub>N<sub>4</sub>, BN, and AlN. Accordingly, any and all modifications, variations, or equivalent arrangements which may occur to those skilled in the art should be considered to be within the scope of the invention as defined in the annexed claims.

What is claimed is:

1. A process for manufacturing metal and ceramic matrix composites comprising the steps of:

a) arc spraying a thin layer of at least one matrix material over a preplaced first layer of a woven fabric reinforcement material;

b) placing an additional layer of woven fabric reinforcement material on a sprayed matrix layer resulting from the previous step;

c) arc spraying a thin layer of said at least one matrix material over said additional layer; and

d) repeating steps b) and c) until a desired object shape and thickness are achieved;

wherein said reinforcement material comprises discontinuous segments of a material from the group consisting of graphite, silicon carbide, alumina, and boron carbide; and

wherein each said reinforcement layer further comprises a plurality of discrete particles which have been coated by a fluidized bed process with a barrier material that does not form a brittle compound with said matrix material.

2. The process of claim 1 further comprising a finishing step to ensure that said composite is homogenous, well bonded, and substantially free of internal voids.

3. The process of claim 2 wherein said finishing step consists of a high-temperature diffusion anneal.

4. The process of claim 1 wherein each of the arc spraying steps a) and c) comprises spraying a plurality of thin layers of said at least one matrix material over the previously deposited thin layer.

5. The process of claim 1 wherein said matrix material comprises one or more metals from the group consisting of aluminum, titanium, nickel, niobium and their alloys.

6. The process of claim 5 wherein said metal is in the form of wire.

7. The process of claim 6 wherein said metal wire is applied as a pre-alloyed mixture of metals from the group consisting of aluminum, titanium, nickel, and niobium.

8. The process of claim 5 wherein said metal is in the form of powder.

9. The process of claim 8 wherein said metal powder comprises a pre-alloyed mixture of metals from the group consisting of aluminum, titanium, nickel, and niobium.

10. The process of claim 8 wherein said metal powder comprises a mixture of powdered metals from the group consisting of aluminum, titanium, nickel, and niobium.

11. The process of claim 1 wherein each said layer of reinforcement material is first coated with a barrier material which does not form a brittle compound with said matrix material.

12. The process of claim 11 wherein said barrier material comprises a refractory metal from the group consisting of V, Cr, Zr, Nb, Mo, Rh, Hf, Ta, W, Re, Os, Th, and Ir.

13. The process of claim 11 wherein said barrier material comprises a metal from the group consisting of Co, Ni, Cu, and Sn.

14. The process of claim 11 wherein said barrier material comprises aluminum.

15. A process for manufacturing metal and ceramic matrix composites comprising the steps of:

a) arc spraying a thin layer of at least one matrix material over a preplaced first layer of a woven fabric reinforcement material;

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- b) placing an additional layer of woven fabric reinforcement material on a sprayed matrix layer resulting from the previous step;
- c) arc spraying a thin layer of said at least one matrix material over said additional layer; and
- d) repeating steps b) and c) until a desired object shape and thickness are achieved;
- wherein said reinforcement material comprises discontinuous segments of a material from the group consisting of graphite, silicon carbide, alumina, and boron carbide; and
- wherein each said reinforcement layer further comprises a plurality of discrete particles which have been coated by dipping into molten metal that does not form a brittle compound with said matrix material.
16. A process for fabricating metal and ceramic composites comprising the steps of:
- a) establishing a first layer of a segmented woven fabric reinforcement material on a form to which said reinforcement material does not adhere;
- b) arc spraying a matrix material onto said first layer to form a composite layer;
- c) applying more of said segmented woven fabric reinforcement material to said composite layer to form a resulting reinforcement layer;
- d) arc spraying more of said matrix material onto said resulting layer of the previous step to form an additional composite layer; and
- e) repeating steps c) and d) ad libitum until a desired thickness and form are achieved;
- wherein each said reinforcement layer further comprises a plurality of discrete particles which have been coated by a fluidized bed process with a barrier material that does not form a brittle compound with said matrix material.
17. The process of claim 16 further comprising a finishing step of high-temperature diffusion annealing.
18. The process of claim 16 wherein in steps a) and c) said segmented reinforcement material is applied by arc spraying.
19. The process of claim 16 wherein steps c) and d) are performed simultaneously by arc spraying using a torch fed by both said segmented reinforcement material and said matrix material.
20. The process of claim 16 wherein steps c) and d) are performed simultaneously by arc spraying with

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separate torches for said segmented reinforcement material and said matrix material.

21. The process of claim 16 wherein said matrix material comprises one or more metals from the group consisting of aluminum, titanium, nickel, and their alloys.

22. The process of claim 16 wherein said segmented reinforcement material comprises ceramic material selected from the group consisting of alumina, silicon carbide, boron carbide, and silicon nitride.

23. The process of claim 22 wherein said segmented reinforcement material comprises short fibers.

24. The process of claim 16 wherein said segmented reinforcement material is first coated with a barrier material which does not form a brittle compound with said matrix material.

25. The process of claim 24 wherein said barrier material comprises a refractory metal from the group consisting of V, Cr, Zr, Nb, Mo, Rh, Hf, Ta, W, Re, Os, Th, and Ir.

26. The process of claim 24 wherein said barrier material comprises a metal from the group consisting of Co, Ni, Cu, Sn and Al.

27. The process of claim 24 wherein said barrier material comprises an insert metal selected from the group consisting of Ag, Au, Pd and Pt.

28. A process for fabricating metal and ceramic composites comprising the steps of:

- a) establishing a first layer of a segmented woven fabric reinforcement material on a form to which said reinforcement material does not adhere;
- b) arc spraying a matrix material onto said first layer to form a composite layer;
- c) applying more of said segmented woven fabric reinforcement material to said composite layer to form a resulting reinforcement layer;
- d) arc spraying more of said matrix material onto said resulting layer of the previous step to form an additional composite layer; and
- a) repeating steps c) and d) ad libitum until a desired thickness and form are achieved;
- wherein each said reinforcement layer further comprises a plurality of discrete particles which have been coated by dipping into molten metal that does not form a brittle compound with said matrix material.

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# United States Patent [19]

Stinson et al.

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[54] **METHOD OF ENHANCING BOND JOINT  
STRUCTURAL INTEGRITY OF SPRAY CAST  
ARTICLE**

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[21] Appl. No.: **794,320**

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[58] Field of Search ..... **427/34; 419/8, 49;  
228/194, 119, 209, 243; 29/889.1, 889.2**

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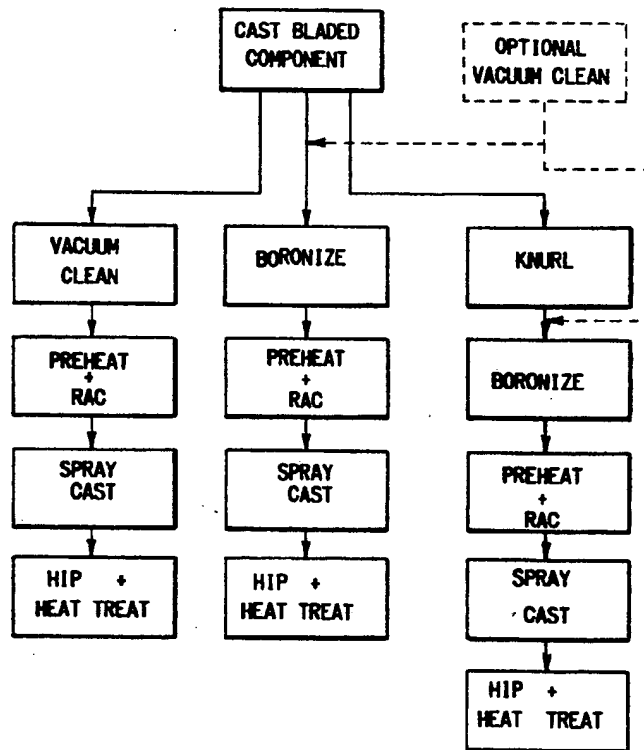
Primary Examiner—Peter A. Nelson

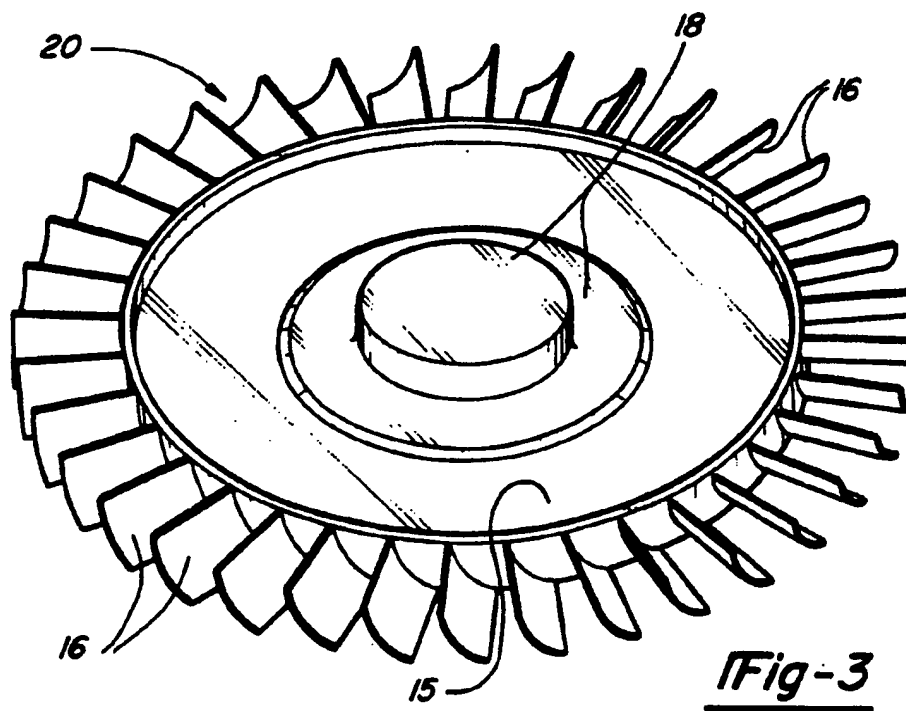
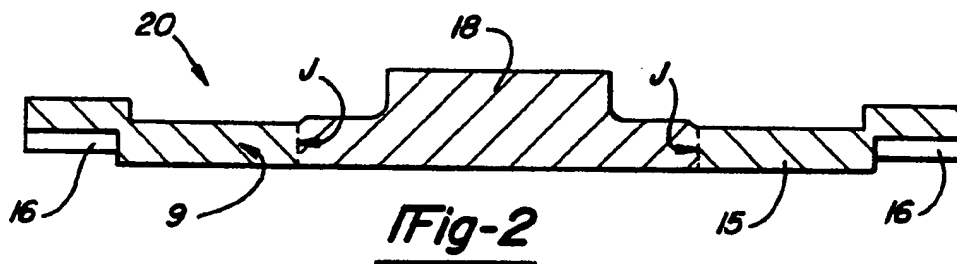
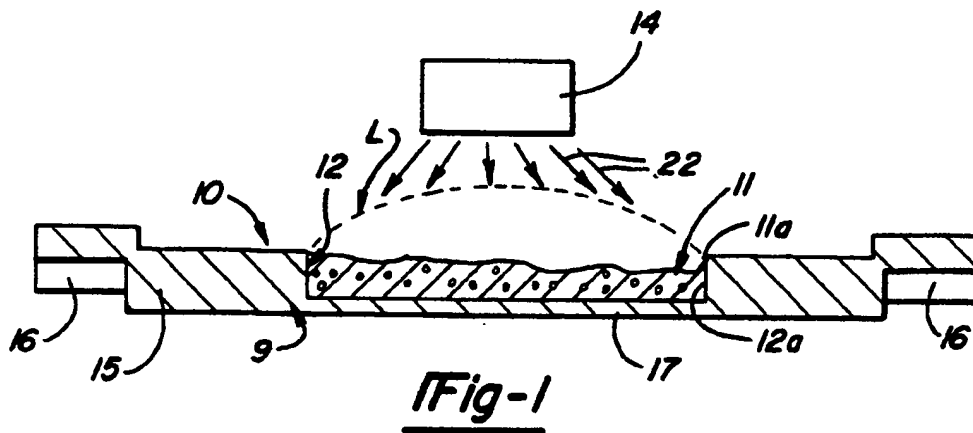
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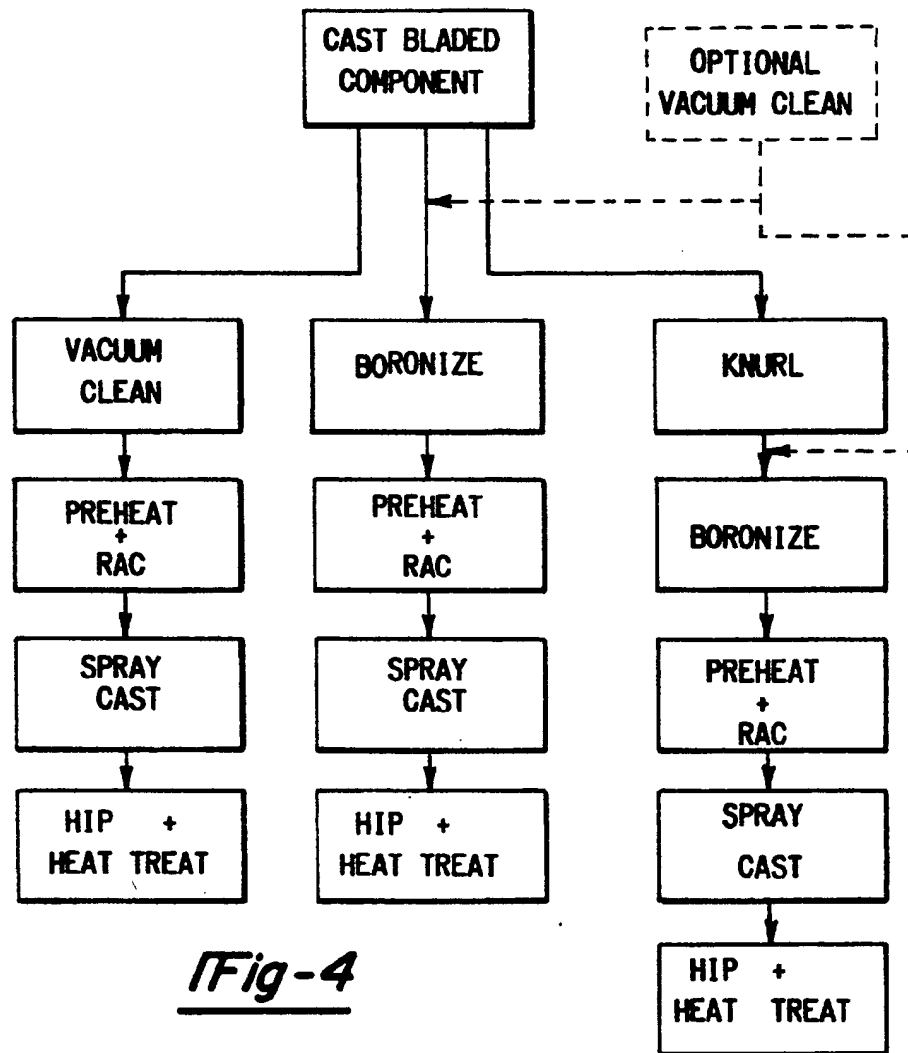
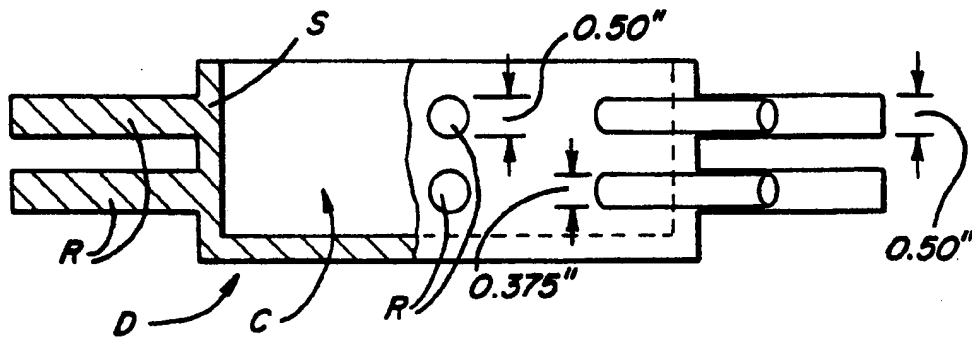
## [57] ABSTRACT

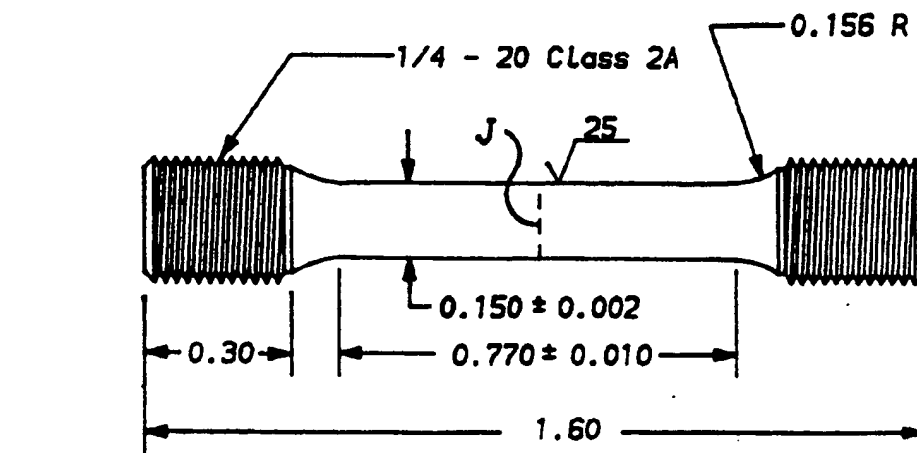
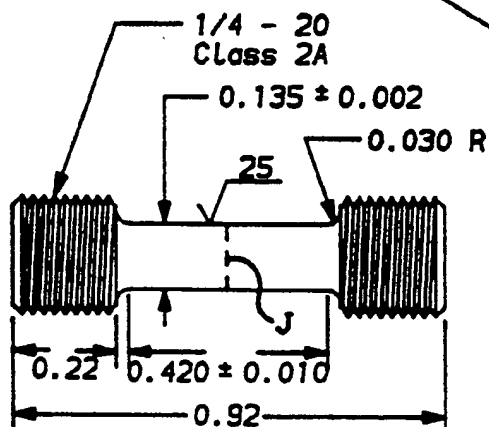
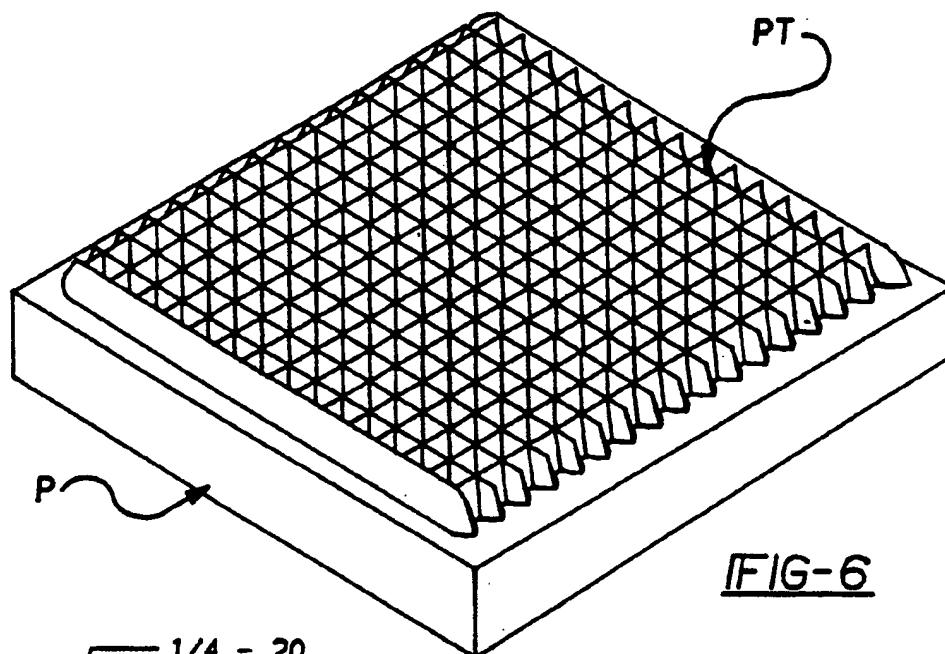
In a method of making a load-bearing article by spray casting a molten metal onto a metal substrate, the substrate surface receiving the spray cast deposit is treated by vacuum cleaning, boronizing and/or knurling to enhance the structural integrity of the diffusion bond joint subsequently formed between the spray cast deposit and the substrate in sustaining a load across the joint without premature joint failure.

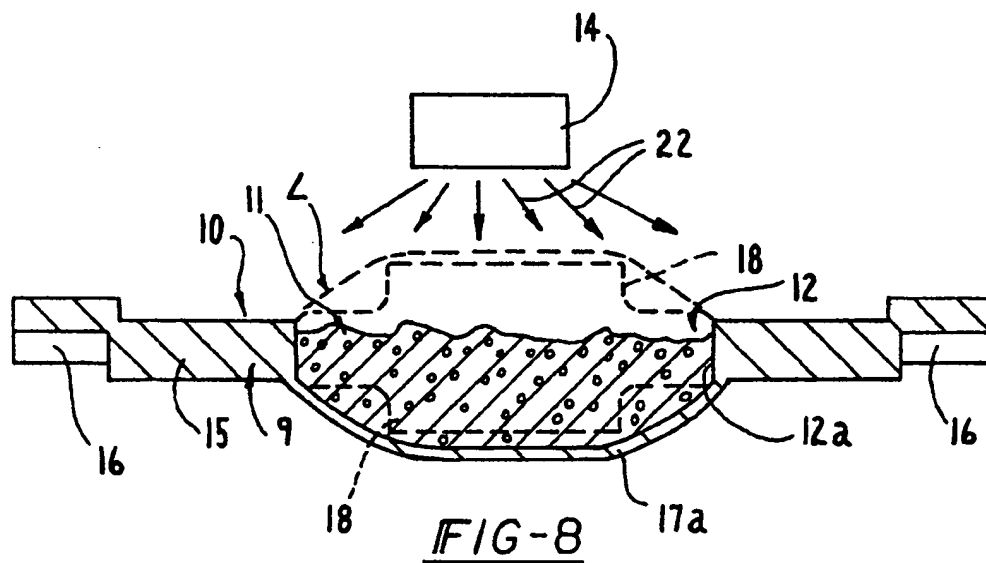
37 Claims, 4 Drawing Sheets





Fig-4Fig-5





# METHOD OF ENHANCING BOND JOINT STRUCTURAL INTEGRITY OF SPRAY CAST ARTICLE

This is a continuation of copending U.S. patent application Ser. No. 07/452,958 filed on Dec. 19, 1989, and now abandoned.

## FIELD OF THE INVENTION

The present invention relates to processes for enhancement of the structural integrity of a metallurgical diffusion bond joint of a structural spray cast article wherein a solid metal substrate and a spray cast metal deposit are diffusion bonded together.

## BACKGROUND OF THE INVENTION

Compressor and turbine rotors (or wheels) as well as centrifugal impellers used in gas turbine engines represent load-bearing components which would have an equiaxed fine grain microstructure in the hub-to-rim regions for optimum low cycle fatigue resistance at service temperature and an equiaxed cast grain, directionally solidified columnar grain or single crystal grain structure in the blades for optimum high temperature stress rupture strength at service temperature.

Although integrally cast bladed turbine rotors have been successfully used for years in many small gas turbine applications, the prior art has recognized that the conventional investment cast rotor inherently compromises the ideal microstructure described above. Namely, the relatively massive hub section of the casting exhibits a coarse, columnar grain structure due to its slower solidification and cooling after casting, while the rim section exhibits a finer, columnar grain structure. As a result of their thin section, the integrally cast blades exhibit a generally equiaxed, finer grain structure. The significance of such a compromise in the microstructure of the turbine rotor becomes apparent when it is recognized that the mechanical properties of the casting are a function of the number and orientation of the grains in the particular region of interest. For example, coarser grain structures are known to offer better elevated temperature stress rupture properties than a fine grain structure. However, the latter grain structure offers better low cycle fatigue properties. Moreover, the low cycle fatigue properties within a cast component depend on the crystallographic orientation of grains relative to the local distribution of stress(es). An unfavorably oriented coarse, columnar grain in a conventionally cast component can contribute to premature fatigue failure of the component.

An improved investment casting process, known as the Grainex® investment casting process, was developed to enhance the uniformity of the microstructure of integrally cast bladed rotors (specifically integral turbine wheels) to meet new challenges of component performance and reliability demanded by increased thrust and horsepower applications. The Grainex process includes motion of the mold during solidification of the melt and also, a post-casting HIP (hot isostatic pressing) treatment. This process develops a substantially uniform fine, equiaxed grain structure through the hub, web and rim regions of the casting. This microstructure provides a significant improvement in the low cycle fatigue properties in these sections of the cast turbine wheel while providing stress rupture properties

in the blades similar to those obtainable in conventionally investment cast bladed rotors.

Another improved investment casting process, known as the MX® investment casting process, was also developed to enhance the uniformity of the microstructure of castings. The MX process involves filling a properly heated mold with molten metal having little superheat (e.g., within 20° F. of its measured melting temperature) and then solidifying the molten metal in the mold at a rate to form a casting having a substantially equiaxed cellular, non-dendritic microstructure uniformly throughout with attendant improvement in the mechanical properties of the casting.

Integrally bladed rotors have also been fabricated by machining processes which utilize either ingot or consolidated metal powder starting stock. The powder metal rotors are generally consolidated by hot isostatic processing (HIP) and demonstrate reduced alloy segregation compared to ingot metallurgy. Powder metal rotors are, however, susceptible to thermally induced porosity (TIP) from residual argon used in powder atomization. Any oxygen contamination of powders can form an oxide network resulting in metallographically detectable prior particle boundaries which are known sites of fracture initiation. These limitations make manufacture of rotors by machining of ingot or consolidated metal powder costly in terms of both processing and quality controls.

Advanced powder metal manufacturing and consolidating techniques coupled with advanced forging processes have provided the capability to produce fine grain rotors which exhibit improved low cycle fatigue properties as compared to conventional investment cast rotors. However, the forged rotors typically exhibit inferior stress rupture properties compared to conventional investment cast rotors.

Unfortunately, in general, metallurgical processing to maximize low cycle fatigue properties of a metal results in reduced creep (stress rupture) properties. As a result, in more demanding service applications where increased thrust and horsepower are required (e.g., in military aircraft), designers have often resorted to the traditional separately bladed/mechanical attachment approach that involves fabricating a fine-grained, forged disk; machining slots in the disk to accept machined blade roots; and inserting cast blades of the desired grain structure (e.g., directionally oriented or single crystal) into the slots. However, machining slots and blade roots are costly processing steps. This method also limits the number of blades that can be attached, especially in smaller engines. A design with a large number of blades often is desirable for higher performance.

Those skilled in the art of turbine engine design have recognized the potential advantages of combining the ease of fabrication and the structural integrity of monolithic integrally cast/forged rotors with the high performance capability obtainable in separately bladed turbine engine rotors. Several approaches have been developed to produce such a turbine rotor. One such approach is illustrated in U.S. Pat. No. 4,096,615 wherein an equiaxed blade ring is cast and then solid state diffusion bonded to a separately produced powder metal hub or disk in a hot isostatic pressing step. Both an interference fit and brazing are usually required to achieve complete bonding during HIP'ing. In particular, a radially inwardly facing surface of the blade ring is machined to precise diameter to form a bonding surface adapted to

mate with the radially outwardly facing bonding surface of a hub or disk made of another material. The blade ring is positioned over the hub and oxygen and other contaminants are removed from the bonding surfaces by vacuum treatment, followed by sealing the external joint lines with braze material. Hot isostatic pressing is then used to diffuse and bond the blade ring to the hub. This approach has the disadvantage of requiring several separate processes: (1) casting the blade ring; (2) precision machining the inner diameter of the blade ring; (3) powder metal HIP consolidation; (4) precision machining the outer diameter of the powder metal hub; (5) assembly of the blade ring and powder metal hub; and (6) a second HIP operation to achieve final solid state diffusion bonding. Each of these processes is expensive and may create additional costs arising from defect scrap losses.

U.S. Pat. No. 4,270,256 describes a somewhat similar process for making a hybrid turbine rotor wherein an expendable blade fixturing ring is used to position the blades for bonding directly to a hub in a hot isostatic pressing step. The blade fixturing ring is removed after the blades are bonded to the hub.

A similar, complex approach for manufacturing a dual-alloy integrally bladed rotor is illustrated in U.S. Pat. No. 4,529,452. In that approach, a blade ring is formed by diffusion bonding a plurality of single crystal elements together. The bonded blade ring is then bonded to a hub by a superplastic forming/solid state diffusion bonding step.

Another approach used in the art employs powder metal in an investment mold which has directionally solidified or single crystal cast blades positioned within it. The mold is loaded in a metal can, covered with an inert pressure-transmitting media, vacuum sealed and hot isostatically pressed. This combined blade/powder metal approach has less process steps than the interference fit approach described immediately above but is severely limited in dimensional control due to blade/mold movement during consolidation of the 65-70% dense powder.

A relatively new low pressure, high velocity plasma spray method to produce fine grain, load-bearing structural components (as opposed to protective coatings on a component) is illustrated in U.S. Pat. Nos. 4,418,124 and 4,447,466. This low pressure, high velocity plasma spray method to produce structural components employs a spraying procedure described in U.S. Pat. No. 3,839,618. Attempts have been made to use the low pressure, high velocity plasma spray technique to fabricate dual alloy turbine wheels. In these attempts, a plasma gun in a dynamic partial vacuum (low pressure) is used to plasma spray molten metal onto a solid metal substrate in the form of an integrally bladed dish-shaped member. In particular, metal powder feedstock is injected into the plasma gun and propelled to the substrate in a carrier gas. A plasma jet deposits molten droplets of the spray cast metal on the surface of the solid substrate where the droplets solidify incrementally until the desired structural shape (e.g., a rotor hub preform) is obtained. The droplets are deposited by line-of-sight to produce simple near-net-shape configurations with a joint between the initial solid substrate (e.g., investment cast substrate) and the spray cast metal deposit. The spray cast deposit can be different in composition and/or microstructure from the initial solid substrate. After deposition of the spray cast metal, the preform is hot isostatically pressed (i.e., HIP'ed) to

substantially eliminate voids primarily in the spray cast metal and diffusion bond the spray cast metal and solid substrate at the bond joint therebetween.

However, in attempts to utilize the low pressure plasma spray method to make dual alloy or dual property turbine wheels, prior art workers have found the diffusion bond joint to exhibit a lack of structural integrity as evidenced by an unexpectedly short life in elevated temperature stress rupture tests. In particular, premature planar failures (bondline fractures) solely through the bond joint have been observed in stress rupture tests where a load is applied across the joint at elevated temperature. In spite of various efforts to facilitate diffusion bonding between the spray cast metal and the metal substrate (the bladed component), the problem of inadequate bond joint structural integrity has persisted.

It is an object of the invention to overcome this problem and to so enhance the structural integrity of the diffusion bond joint formed between the spray cast metal and the solid substrate that premature bond joint failures in elevated temperature stress rupture tests (simulating intended service conditions) are reduced or substantially eliminated and result in acceptable bond joint life under both testing and service conditions.

It is another object of the invention to subject the metal substrate receiving the spray cast metal to surface treatment processes that can be used individually or in various combinations with subsequent hot isostatic compaction to enhance bond joint integrity depending upon the degree of compositional difference between the metal substrate and spray cast metal deposit bonded thereto.

It is still another object of the invention to provide such bond joint enhancement processes which overcome the many limitations/disadvantages associated with the other known methods of fabricating dual-property, diffusion bonded bladed rotors.

#### SUMMARY OF THE INVENTION

The invention envisions an improved method of making a structural (load-bearing), multi-property article wherein a molten metal is spray cast on a metal substrate and the spray cast metal deposit and the substrate are treated so as to form a metallurgical diffusion bond joint therebetween. In particular, the invention contemplates enhancing the structural integrity of the diffusion bond joint in sustaining a load thereacross in service without exhibiting failure solely in the metallurgical diffusion bond joint between the substrate and the deposit.

The invention contemplates subjecting the surface of the solid metal substrate to one or more surface treatments in selected sequence with low pressure, high velocity plasma spray casting of the molten metal thereon (either fully or partially molten droplets/particles) such that the surface treatments, preferably in conjunction with subsequent hot isostatic pressing of the substrate and spray cast deposit, enhance the structural integrity of the diffusion bond joint between the substrate and the spray cast deposit. The invention also contemplates employing the surface treatments individually or in various combinations depending on the degree of similarity or dissimilarity of the compositions of the spray cast metal and the substrate.

In a typical working embodiment of the invention for improving the structural integrity of the diffusion bond joint between a substrate and a spray cast deposit of

dissimilar compositions (e.g., a dual alloy article), the method involves heating the substrate surface in the presence of a melting point depressant, preferably a boron-bearing layer at the substrate surface, such that an exposed in-situ liquid phase layer is formed on the surface. The molten metal is then sprayed onto the exposed in-situ liquid phase to incrementally build-up a solidified spray cast deposit on the substrate surface. The spray cast deposit and the substrate are then hot isostatically pressed in such a manner as to enhance the metallurgical diffusion bond, preferably to the extent of promoting epitaxial grain growth across the interfacial bond region between the substrate and the spray cast deposit, to enhance the structural integrity of the metallurgical diffusion bond joint in sustaining a load thereacross without exhibiting failure solely in the bond joint and to fully densify the spray cast material. A structural, multi-property article is thereby formed in accordance with this working embodiment of the invention.

In a preferred practice of this working embodiment of the invention, the substrate surface is heated and then reverse arc cleaned to form the exposed in-situ liquid phase thereon acceptable for receiving the spray cast deposit. In another preferred embodiment, the substrate surface is knurled prior to applying the melting point depressant thereon. Knurling of the substrate surface forces any interfacial crack formed in proximity thereto in the structural article under loading to deviate from a strictly planar path, thereby requiring increased energy for the crack to propagate in the interfacial bond region between the bonded substrate and deposit of the article.

In another typical working embodiment of the invention for improving the structural integrity of the diffusion bond joint between a substrate and a spray cast deposit of the same or similar compositions, the method involves initially vacuum cleaning the substrate surface by exposure to a vacuum of at least  $10^{-4}$  torr at a suitable elevated temperature prior to spray casting. Then, the substrate surface is heated and reverse arc cleaned in the spray chamber immediately prior to spray casting the molten metal thereon. The spray cast deposit and the substrate are thereafter hot isostatically pressed to provide the desired metallurgical diffusion bond joint therebetween to form the structural article.

In the embodiments of the invention described hereinabove, the substrate advantageously comprises an equiaxed, single crystal or directionally solidified columnar grain metal member while the spray cast deposit comprises an equiaxed fine grain microstructure.

In an exemplary embodiment of the invention, the equiaxed, single crystal or columnar grained metal member may comprise a bladed dish-shaped component of a turbine rotor while the fine grained spray cast deposit may comprise the hub of the turbine rotor. A multi-property structural article (e.g., turbine rotor) is thereby provided in accordance with the invention.

The invention is effective to improve the structural integrity of the metallurgical diffusion bond joint in such structural, multi-property articles. Preferably, the integrity of the diffusion bond joint is improved to such an extent that the bond joint can sustain a load thereacross under intended service conditions without exhibiting failure solely in the joint. That is, the bond joint is not a preferential failure site of such articles.

The aforementioned objects and advantages of the invention will become more apparent from the following detailed description taken with the drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view of a solid metal substrate in the form of a bladed dish-shaped component, shown in section, and a plasma spray nozzle for spray casting molten metal in the cavity of the substrate.

FIG. 2 is a schematic sectional view similar to FIG. 1 of the structural article (turbine wheel) formed by the method of the invention after machining the spray cast deposit to form a hub of a turbine wheel.

FIG. 3 is a perspective view of turbine wheel made in accordance with the invention.

FIG. 4 is a process flow chart of the invention.

FIG. 5 is side elevation, partially broken away, of a spoked dish-shaped specimen (i.e., a pseudo turbine wheel test specimen) in which the spray cast deposit is received.

FIG. 6 is a perspective view of a plate specimen showing a typical pyramidal knurl pattern on the top surface adapted to receive the spray cast metal.

FIGS. 7A and 7B illustrate stress rupture test specimens (with dimensions shown) used in the examples set forth herein.

FIG. 8 is a schematic view similar to FIG. 1 of another embodiment of the invention.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described in terms of certain embodiments that are illustrative of the invention.

The invention relates to a method of making a structural, multi-property article by spraying molten metal onto at least one solid metal substrate using low pressure, high velocity plasma spraying procedures similar to those described in U.S. Pat. Nos. 3,839,618; 4,418,124 and 4,447,466. The method finds particular utility in making structural, multi-property articles for service at high temperature and can be used to form metal articles having different microstructures in different locations. For example, a multiple property turbine wheel or rotor having a fine grained hub and single crystal, directionally solidified or cast equiaxed grain blades can be fabricated in accordance with the invention.

Although the detailed description and examples set forth hereinbelow are directed to manufacture of multi-property turbine wheels or rotors, the invention is not so limited and may be employed in the manufacture of myriad other structural, multi-property articles. Moreover, although the detailed description and examples set out hereinbelow are directed to nickel-base superalloys, the invention is not so limited and is operable with other superalloys as well as other metal and alloy systems that are capable of being formed into a molten metal spray and solidified to form a structural article that can have useful properties imparted thereto through appropriate thermal treatments.

In accordance with the invention, the first step of the method is to provide a solid metal substrate 10, see FIG. 1, adapted to both receive the molten metal being sprayed on its surface and to solidify the spray cast metal in the appropriate shape and microstructure.

As here embodied and depicted in FIG. 1, the solid metal substrate 10 preferably comprises a bladed dish-shaped component 9 of a turbine engine rotor. The bladed dish-shaped component 9 includes a cylindrical (or other shape) cavity 12 for receiving the spray cast metal deposit as described in detail hereinbelow. The

cavity 12 is formed by a rim section 15 and a bottom wall 17. The bottom wall 17 as well as portions of the spray cast metal 11 are removed (e.g., machined off) in subsequent processing to yield the turbine rotor 20 (e.g., see FIGS. 2 and 3). The rim section 15 includes a plurality of circumferentially spaced apart integral blades 16 which may have a microstructure uniquely suited to the conditions imposed on the blades in service (e.g., the blades 16 may have an equiaxed, directionally solidified or single crystal microstructure depending upon the intended service conditions for the rotor 20). The cylindrical surface 12a of the cavity 12 receives the molten metal deposit 11 sprayed thereon from a plasma spray nozzle 14 (schematically depicted). The spray cast deposit 11 is built up above the cavity 12 to a level L (see phantom line in FIG. 1) such that the hub 18, FIGS. 2 and 3, can be machined from the deposit.

Referring to FIG. 8 wherein like features of FIG. 1 are represented by like reference numerals, an alternate configuration for the bladed dish-shaped component 9 of FIG. 1 is shown. Namely, the dish-shaped component 9 of FIG. 8 includes a downwardly bowed or arcuate, removable bottom wall 17a to receive sufficient spray cast metal 11 to be machined into a central hub 18 (see phantom lines) extending axially on opposite sides of the rim section 15.

The invention envisions forming a metallurgical diffusion bond joint J, FIG. 2, of enhanced structural integrity between the metal substrate 10 (or bladed component 9) and the spray cast metal 11. A metallurgical diffusion bond joint is a continuous metallic structure of commingled atoms across the interface of the substrate 10 and the spray cast metal 11 being joined. The presence of epitaxial grain growth across the interface is considered to evidence a preferred, optimized metallurgical diffusion bond joint and to infer that the substrate surface 12a is atomically clean just prior to spraying of the spray cast metal 11 thereon.

In FIGS. 2 and 3, the spray cast metal deposit 11 is shown machined to form the hub 18 of the gas turbine rotor 20. An axially-extending passage (not shown) may be ultimately machined in the hub 18 to receive the drive shaft of the gas turbine engine in known manner.

In accordance with the invention, the formation of a diffusion bond joint J of enhanced structural integrity between the surface 12a of the metal substrate 10 and the spray cast metal 11 is effected by applying one or more surface treatments (to be described) to the surface 12a of the cavity 12 in proper sequence with spray casting of the molten metal 11 thereon and subsequent hot isostatic pressing of the substrate and spray cast deposit. The intent of the surface treatments is to reduce and possibly eliminate the presence of certain tramp elements, such as S, Si, O, P, etc. in a substrate surface layer to hinder or prevent migration of such tramp elements to the substrate surface 12a and to the subsequently formed bond joint J during preheating of the substrate 10 prior to spray casting and during subsequent heating cycles. The invention involves the discovery that in structural spray cast articles made prior to this invention, such tramp elements were present at the bond joint J (as verified by Auger electron surface analysis) and adversely affected the bond joint structural integrity as measured by mechanical properties, specifically elevated temperature stress rupture properties.

The surface treatments of the present invention used to minimize the presence of these undesirable elements

at the substrate surface 12a and at the diffusion bond joint J to enhance the bond joint integrity include the following:

(a) Vacuum cleaning the surface 12a at elevated temperature under a relatively hard vacuum; e.g., a vacuum of at least about  $10^{-4}$  torr, preferably about  $10^{-5}$  to about  $10^{-6}$  torr, to vaporize the undesirable elements from the cavity surface 12a. The vacuum cleaning treatment typically involves positioning the substrate 10 in a vacuum furnace (not shown) and evacuating the furnace to at least about  $10^{-4}$  torr, preferably  $10^{-5}$  to  $10^{-6}$  torr, while the substrate 10 is heated to a sufficiently high temperature, such as preferably greater than 2000° F. for nickel base superalloys, and for a sufficient time (e.g., 3 hours) to vaporize or otherwise remove the undesirable elements S, Si, O, P etc. from a surface layer of the cavity surface 12a. Typically after vacuum cleaning, the substrate is placed in a clean, sealed plastic bag for transport to the low pressure plasma spray chamber or, if the substrate is to be boronized (as will be described hereinafter) to a boronizing facility and thereafter to the low pressure plasma spray chamber.

(b) Boronizing of the substrate surface 12a to form, upon subsequent preheating and reverse arc cleaning, an exposed in-situ liquid phase or layer on the surface 12a at the onset of spray casting to receive the spray cast deposit and to prevent embrittlement at the interfacial region between surface 12a and the spray cast deposit 11 by oxygen and other tramp elements. During the molten stage, boron acts as a fluxing agent for the surface 12a. The in-situ molten layer acts to enhance bonding at the spray deposit-to-substrate interface by allowing liquid state diffusion kinetics to occur for some period of time. Such liquid state diffusion occurs at a rate approximately 100 times greater than solid state diffusion. The boron can be diffused into the substrate surface 12a to form a boron-bearing surface layer by various techniques, for example, by chemical vapor deposition or by over-the-pack gas phase deposition. The quantity of boron applied to the substrate surface 12a will depend on the compositions of the substrate metal and spray cast metal involved as well as the substrate temperature prior to spray casting. For nickel base superalloys to be preheated to about 2000° F. to about 2150° F. immediately prior to spray casting, the boron is applied (as applied by Materials Development Corp., Medford, Mass.) to the substrate surface 12a in the range of about 2 mg/in<sup>2</sup> (0.3 mg/cm<sup>2</sup>) to about 17 mg/in<sup>2</sup> (2.6 mg/cm<sup>2</sup>), preferably about 4 mg/in<sup>2</sup> (0.6 mg/cm<sup>2</sup>) to about 6 mg/in<sup>2</sup> (0.9 mg/cm<sup>2</sup>). In particular, the quantity of boron present and the temperature of the substrate 10 are selected to generate an exposed in-situ liquid phase at the onset of spray casting. This liquid phase has been found to enhance the metallurgical diffusion bond developed between the substrate 10 and the spray cast metal 11. The boron functions as a melting point depressant such that heating of the surface 12a to the selected preheat temperature effects incipient surface melting and fluxing of the substrate surface 12a.

Those skilled in the art will appreciate that selection of quantity of boron and the temperature of the substrate 10 for achieving incipient melting also will be a function of the composition of the substrate 10 and to some extent the configuration of the substrate 10. The desired substrate temperature can be obtained by preheating using a thermal plasma impinged on the substrate surface 12a followed by reverse arc cleaning of

the substrate surface 12a as will be described hereinbelow. It is the reverse arc cleaning process which both cleans the substrate surface of oxide contamination formed during the preheat cycle, and provides the additional energy to form in-situ the exposed molten layer just before the onset of low pressure, high velocity plasma spray casting. That is, the surface energy input afforded by reverse arc cleaning causes the surface temperature to exceed the melting point of the boron alloyed surface layer, thereby allowing surface melting.

(c) Knurling the substrate surface 12a to render the interface convoluted rather than planar, thereby mechanically strengthening the metallurgical diffusion bond joint J by altering the path of propagation of any interfacial crack. Knurling of the substrate surface 12a can be employed in combination with the boronizing treatment (b) with or without the vacuum cleaning treatment (a) described hereinabove. If the vacuum cleaning treatment (a) is employed with the boronizing treatment (b), the substrate is knurled first and then subjected to the treatments (a) and (b) in succession.

A typical pyramidal knurling pattern PT is shown in FIG. 6 for test specimens to be discussed hereinbelow. A spiral threaded knurling pattern as well as other knurling patterns characterized by surface apexes can also be used. Knurling of the substrate surface 12a can be effected by casting the surface with the desired features, machining the surface, rolling the surface 12a with a suitably configured forming die as well as other techniques. The end result or goal of the knurling pattern is to provide a convoluted substrate surface 12a with numerous apexes rather than planar characteristics. Typical dimensions of a pyramidal knurling pattern are set forth in the examples provided hereinbelow.

(d) Various combinations of treatments (a)-(c) set forth above can be used as desired to achieve the required enhancement of the structural integrity of the metallurgical diffusion bond joint J between the substrate 10 and the spray cast metal 11, for example, as measured by elevated temperature stress rupture tests.

With respect to treatments (a)-(d) set forth above, the present invention involves the further discovery that different surface treatments have different effects on bond joint structural integrity depending upon the similarity or dissimilarity of the compositions of the substrate metal and the spray cast metal. In particular, when the composition of the substrate metal and the spray cast metal are the same or similar, the vacuum cleaning treatment, alone, has been found to substantially enhance the structural integrity of the bond joint as illustrated in the examples set forth hereinbelow. On the other hand, for dissimilar compositions, the boronizing/heating treatment, with or without knurling, but with development of the exposed molten layer has been found to substantially enhance the structural integrity of the bond joint as illustrated in the examples set forth hereinbelow.

In accordance with the invention, the molten metal is sprayed onto the surface 12a of the solid (e.g., cast) metal substrate 10 after the surface 12a is subjected to one or more of the aforementioned surface treatments (a)-(d) referred to hereinabove depending upon the compositional similarities or dissimilarities between the substrate and the spray cast deposit, and after preheating and cleaning of the surface 12a as described hereinbelow.

As here embodied and depicted schematically in FIG. 1, there is provided a plasma spray nozzle 14 for

projecting sprayed molten metal (represented by arrows 22) onto surface 12a of the cavity 12. Preferably, the molten metal 22 is sprayed by means of the introduction of metal powder (e.g., -325 mesh) into a high velocity thermal plasma. Particular success has been experienced using a plasma spray apparatus manufactured by Electro Plasma Inc., of Irvine, Calif. Such an apparatus generates a high temperature plasma of flowing inert gas. Solid metal powder is injected into and fully or partially melted by the high temperature plasma and the resulting fully or partially molten droplets/particles are projected, by movement of the plasma, toward the substrate surface 12a that is prepared to receive them. To ensure a uniform deposition of the sprayed molten metal onto the surface 12a of the solid metal substrate, the solid metal substrate 10 may be moved and/or the plasma gun indexed in order to impart a configuration to the deposited metal appropriate for the particular application. The spray cast metal 11 is adherent to the substrate surface 12a to form a preform comprising the spray cast metal 11 deposited and incrementally solidified onto the solid metal substrate 10. An as-sprayed metallurgical diffusion bond is formed between the substrate 10 and the spray cast deposit 11 as well as throughout the spray cast deposit 11.

As depicted in FIGS. 1 and 2, the nozzle 14 is in a fixed position with respect to the cavity 12 and the substrate 10 is rotated with respect to the nozzle 14 to deposit the metal 11 within and above the cavity 12 in the appropriate configuration (e.g., to level L). Where the cavity 12 receiving the molten metal 22 has an irregular configuration, it may be necessary to move both the solid metal substrate 10 as well as the nozzle 14 in order to minimize the formation of voids at the interface between the surface 12a and the spray cast metal 11. Because the process is conducted with a controlled inert atmosphere (e.g., Ar and He), the surface 12a of the cavity 12 and the surface of the spray cast deposit 11 should be free of surface contamination. A subsequent hot isostatic pressing operation is used to close any minor voids at the interface, fully densify the deposit 11 and enhance the as-sprayed metallurgical diffusion bond joint between the spray cast deposit 11 and the solid metal substrate 10.

In a preferred embodiment of the invention, prior to low pressure, high velocity spray casting in the spray chamber, the substrate 10 is preheated in the spray chamber in a controlled, low pressure atmosphere (Ar and He) by impingement with a thermal plasma and the substrate surface 12a is then immediately reverse arc cleaned (RAC'ed) in a thermal plasma. Preheating of the solid metal substrate affects the rate of heat transfer when the molten metal spray subsequently strikes the substrate surface 12a on which it is deposited. Because steep thermal gradients between the spray cast deposit and the substrate can result in residual stresses across their interface, the amount of preheating is controlled to minimize such gradients. For nickel-base alloys, preheating the solid metal substrate to a temperature in the range of from 2000° F. to 2200° F. is preferred. The solid metal substrate 10 can be preheated by means of the thermal plasma or other means (e.g., induction heating) prior to the deposition of the spray cast metal 11, thereby providing an efficient production process capable of being automated.

The reverse arc cleaning process is described in an article *Journal of Metals*, October 1981, authored by Shankar et al and involves forming a direct current arc

with the substrate surface 12a as the cathode. Reverse arc cleaning removes surface impurities when conducted in a controlled atmosphere at low pressure as explained in copending U.S. patent application Ser. No. 173,468 of common assignee herewith, the teachings of which are incorporated herein by reference.

The spray chamber (not shown) receiving the substrate 10 is typically first evacuated to about 1-15 microns Hg, and then backfilled to 30-50 torr with Ar and He. The substrate 10 is then preheated to a desired preheat temperature by impinging a thermal plasma generated by the nozzle 14 on the surface 12a. Reverse arc cleaning (RAC) is carried out generally by maintaining the arc at about 100-250 amps between the spray nozzle gun (anode) and the substrate surface (cathode) 12a at a chamber pressure in the range of about 30 to about 70 torr. Both preheating and reverse arc cleaning are conducted in the controlled atmosphere of argon and helium. The substrate surface 12a can be preheated and then reverse arc cleaned (RAC) in multiple sequences prior to spray casting. However, only the final reverse arc clean (RAC) step (just prior to the onset of spray casting) should be allowed to form the exposed in-situ molten phase or layer when the substrate is boronized. The time of RAC can be used to control cleaning of the substrate surface 12a and uniformity of the molten layer formed.

The molten metal sprayed onto the substrate surface 12a is rapidly solidified because of the temperature differential between the sprayed molten metal and the solid metal substrate 10 even when the solid metal substrate 10 is preheated. This affords the opportunity to control the microstructure of the spray cast metal 11. By controlling the deposition rate onto the solid metal substrate, the gas pressure in the spray chamber, the velocity of the molten metal spray, and the temperature differential between the metal spray and the solid metal substrate, the grain size of the spray cast metal 11 can be varied and controlled. The molten metal solidifies incrementally to the solid metal substrate 10 and then to the previously deposited solidified spray cast metal 11 to build up the spray cast metal deposit on the substrate 10.

The spray cast metal 11 is subsequently rendered fully dense with a desired fine grain size (e.g., in the range of from ASTM 4 to ASTM 10) by appropriate thermal treatments. This grain size range generally meets the grain size requirements of the hub of turbine engine rotors.

In particular, after depositing the spray cast metal 11 on the substrate 10, the preform thusly formed is hot isostatically pressed to virtually eliminate any voids in the spray cast metal 11 and metallurgically diffusion bond the spray cast metal 11 and the surface 12a of the solid metal substrate 10. Hot isostatic pressing is preferably conducted in such a manner as to promote epitaxial grain growth across the interfacial bond region between the substrate surface 12a and the spray cast metal 11. As is well known, hot isostatic pressing is carried out under gas pressure thereby applying an isostatic pressure on the preform. After consolidation of the preform by hot isostatic pressing, the preform can be heat treated to obtain the desired mechanical properties for both the spray cast metal 11 and the solid metal substrate 10.

The process of the invention includes the formation during the final stages of spray casting of a gas impervious layer on the outermost surface (i.e., uppermost surface in FIG. 1) of the spray cast metal 11 to allow removal of residual microporosity by the subsequent hot

isostatic pressing treatment. The gas impervious layer provides a means of transmitting the gas pressure during hot isostatic pressing to densify the spray cast metal 11 and eliminate any residual voids therein. Moreover, there will be a gas impervious bond between the outer exposed edge 11a of the spray cast metal 11, FIG. 1, and the cavity 12 shown so that gas pressure applied during hot isostatic pressing does not infiltrate to the interfacial region between the spray cast metal 11 and the cavity 12.

In general, the present invention is practiced with isostatic pressures of 15 to 25 KSI at temperatures of between about 1950° F. to about 2250° F. for about 2 to about 4 hours when the substrate and the spray cast metal are typical nickel base superalloys.

As mentioned hereinabove, the invention involves the discovery that the different surface treatments (a)-(d) described hereinabove have different effects on the structural integrity of structural spray cast articles depending upon the similarity or dissimilarity of the compositions of the substrate metal 10 and the spray cast metal 11. In particular, a set of preliminary tests was conducted to spray cast low carbon Astroloy (LC Astroloy) nickel base superalloy onto an investment cast Mar-M247 nickel base superalloy substrate as representative of dissimilar compositions. Another set of preliminary tests was conducted to spray cast LC Astroloy onto a LC Astroloy substrate as representative of the same or similar compositions. The LC Astroloy substrate itself had been spray cast and hot isostatically pressed under the same spraying and pressing conditions as described hereinafter for the specimens.

The following Table sets forth the compositions of superalloy specimens described hereinbelow in the examples.

TABLE

Element	ALLOY COMPOSITIONS		
	Cast IN713LC	VPSPD* LC ASTROLOY	Cast MAR-M247
Carbon	0.06	0.03	0.16
Chromium	12.00	15.00	8.20
Tungsten	—	—	10.00
Iron	—	—	—
Cobalt	1.00	17.00	10.00
Molybdenum	4.30	5.00	0.60
Aluminum	5.80	4.00	5.50
Titanium	0.70	3.50	1.00
Columbium	Cb + Ta	—	—
Tantalum		—	3.00
Zirconium	0.06	—	0.05
Boron	0.007	0.020	0.015
Vanadium	—	—	—
Hafnium	—	—	1.50

\*vacuum plasma structural deposition

#### Testing Of Dissimilar Compositions

For the test set involving the dissimilar compositions (i.e., LC Astroloy spray cast on Mar-M247), specimens were prepared (as described in detail hereinbelow) to investigate the effect of 1) vacuum cleaning, 2) heating a boronized substrate surface 12a and 3) knurling plus heating a boronized substrate surface 12a on the structural integrity of the bond joint J of structural spray cast specimens. In these tests, the investment cast Mar-M247 substrate comprised a generally flat, square plate of nominal 2 inches (5 cm) width, 2 inches (5 cm) length and  $\frac{1}{4}$  inch (1.9 cm) thickness. A knurled specimen plate P is shown in FIG. 6.

The substrate surface 12a typically was solvent cleaned (e.g., using 1,1,1-trichloroethane and then Freon solvent) prior to vacuum cleaning and/or boronizing.

The LC Astroloy was spray cast to a thickness of about  $\frac{1}{8}$  inch (1.9 cm) onto the Mar-M247 substrate plate as it was rotated with the nozzle 14 perpendicular to the substrate plate. The spray gun was translated relative to the rotating substrate to insure build-up of a uniform deposit in the cavity 12.

Prior to molten metal spraying, the specimen plate was low pressure plasma preheated (LPP) with the plasma gun at a chamber pressure of about 40 torr (Ar and He) with a gun power of approximately 70 KW until a surface temperature of 1000° F. was observed as indicated by the pyrometer. Then, the preheated specimen plate was low temperature reverse arc cleaned (LT RAC) at 1000° F. at about 125 amps until clean. For specimens that were previously boronized, no molten layer was formed during the LT RAC.

The LPP preheat of the specimen plate was continued at 50 torr until the temperature of the plate surface was about 2160° F. At about 2160° F., a high temperature reverse arc clean (HT RAC) was initiated. For specimens that were boronized, the HT RAC was maintained until the surface was observed to be clean (e.g., substantially free of any oxides formed during preheating) and a uniform molten surface layer was observed thereon. The HT RAC treatment provides the required surface energy input to clean the specimen and, if it is boronized, to also melt the boronized surface layer.

The HT RAC was turned off and powder feeding into the existing plasma plume was immediately started to impinge fully molten droplets on the plate surface with a spray chamber pressure of about 10 microns or less. A zero time lag between HT RAC "off" and powder feed "on" is desired.

Following plasma spraying the plate was cooled under a vacuum of less than 10 microns. The chamber was then argon backfilled to atmosphere prior to specimen removal.

After cooling, the spray cast preforms were hot isostatically pressed at 2165° F. and 25 KSI for 4 hours. Thereafter, the preforms were heat treated as follows:

2040° F. for 2 hours/AC (air cool)+1600° F. for 8 hours/AC+1800° F. for 4 hours/AC+1200° F. for 24 hours/AC+1400° F. for 8 hours/AC to ambient temperature.

Table I sets forth 1400° F./80 ksi stress rupture test results for the surface treatments (a)-(d) of the invention described hereinabove for the aforementioned dissimilar compositions. The configuration of the stress rupture specimens is shown in FIG. 7A. The stress rupture specimens are machined from the center of the spray cast plates P with the longitudinal axis of the stress rupture specimens normal to the plate surface such that the diffusion bond joint is normal to the longitudinal axis of the stress rupture specimens (e.g., see FIG. 7A), and centered in the gage section.

The Group I specimens involved only vapor honing of the substrate surface 12a using commercially available alumina grit prior to preheating and reverse arc cleaning. The Group II specimens were vacuum cleaned in accordance with surface treatment (a) set forth above (e.g., vacuum level of at least  $10^{-4}$  torr for 3 hours at 2150° F.). The specimens of Groups II and IV were boronized in accordance with surface treatment (b) set forth above; e.g., 4 mg/in<sup>2</sup> (0.6 mg/cm<sup>2</sup>) to 17 mg/in<sup>2</sup> (2.6 mg/cm<sup>2</sup>) boron was applied to the substrate surface 12a by Materials Development Corp., Medford, Mass. to yield a diffused boron enriched surface layer at the substrate surface 12a. However, the Group IV specimens were heated sufficiently to form a uniform exposed molten layer on the substrate surface at the onset of spray casting whereas the Group III specimens were not so heated and did not develop the uniform exposed molten layer. The specimens of Group V were treated similarly to the Group IV specimens but the substrate surface was knurled prior to being boronized; e.g., the specimens had a 0.04 in.×0.04 in.×0.04 in. (0.10 cm×0.10 cm×0.10 cm) pyramidal knurl pattern, FIG. 6. Specimens of Groups VI and VII were both vacuum cleaned and boronized in accordance with the surface treatments (a) and (b) set forth above. However, the Group VI specimens were heated sufficiently to form the exposed molten layer on the substrate surface at the onset of spray casting whereas the Group VII specimens were not so heated.

TABLE I

VPD LC Astroloy to Cast Mar-M247  
Flat Plate Bond Data

Mar-M247 Surface Prep Method	Sample	Test Parameters	Individual Bar Data			Average Data			Fracture Comments
			Life (hrs)	% EL	% RA	$\bar{x}/\sqrt{n-1}$	% EL $\bar{x}/\sqrt{n-1}$	% RA $\bar{x}/\sqrt{n-1}$	
I Vapor Honed Only (No Boronizing, No Vac Clean, No Molten Layer, No Knurls)	1876/1878	1400° F./80 ksi	21.5	1.6	1.2	20.8/5.7	1.9/0.2	1.9/0.8	Bond Line Failure
			23.7	2.0	1.3				Bond Line Failure
			12.6	1.8	2.4				Bond Line Failure
			25.3	2.0	2.7				Bond Line Failure
II Vacuum Cleaned Only (No Boronizing, No Molten Layer, No Knurls)	1911	1400° F./80 ksi	33.7	2.5	5.6	32.1/1.4	2.0/0.4	5.2/0.4	Bond Line Failure
			30.9	1.8	5.1				Bond Line Failure
			31.8	1.8	4.8				Bond Line Failure
III Boronized Only (No Molten Layer)	1906	1400° F./80 ksi	25.3	1.1	2.1	26.8/1.3	1.7/0.7	2.7/0.7	Bond Line Failure
			27.3	1.6	3.5				Bond Line Failure
			27.7	2.5	2.4				Bond Line Failure
IV Boronized + Molten Layer (No Vac Cleaning, No Knurling)	1921	1400° F./80 ksi	50.5	3.1	4.0	56.1/6.2	3.0/0.1	7.3/3.3	Mixed Mode Failure
			54.9	2.9	10.6				Parent Metal Failure
			62.8	2.9	7.4				Mixed Mode Failure
V Knurling + Boronizing +	1922	1400° F./80 ksi	72.2	6.6	5.1				Mixed Mode Failure

TABLE I-continued

VPSD LC Astroloy to Cast Mar-M247 Flat Plate Bond Data									
Mar-M247 Surface Prep Method	Sample	Test Parameters	Individual Bar Data			Average Data			Fracture Comments
			Life (hrs)	% EL	% RA	Life $\bar{x}/\sqrt{n}-1$	% EL $\bar{x}/\sqrt{n}-1$	% RA $\bar{x}/\sqrt{n}-1$	
Molten Layer (No Vac Cleaning)			56.8	7.8	16.4	67.2/9.0	8.2/1.9	12.9/6.8	Parent Metal Failure
			72.7	10.3	17.4				Parent Metal Failure
VI Vacuum Clean + Boronized + Molten Layer (No knurls)	1973	1400° F./80 ksi	42.9	4.7	13.7				Parent Metal Failure
			67.2	4.0	5.0	59.5/14.4	5.2/1.5	9.5/4.4	Mixed Mode Failure
			68.3	6.9	9.9				Parent Metal Failure
VII Vacuum Clean + Boronize (No Molten Layer, No Knurls)	1959	1400° F./80 ksi	19.1	2.0	0.4	19.4/0.4	1.6/0.6	1.3/1.3	Bond Line Failure
			19.6	1.1	2.2				Bond Line Failure

Note:

El is elongation, RA is reduction in area,  $\bar{x}$  is an average,  $\sqrt{n}-1$  is sample standard deviation

From Table I, it can be seen by comparing surface treatments I and II that the vacuum cleaning treatment by itself results in improvements in metallurgical diffusion bond joint strength properties. A comparison of surface treatments I and III reveals a slight improvement in diffusion bond joint properties resulting from heating the boronized substrate without formation of an exposed molten surface layer. However, from a comparison of surface treatments II and III, it is evident that the vacuum cleaning treatment by itself provides better metallurgical diffusion bond joint properties than heating the boronized substrate without molten layer formation.

The effect of heating the boronized substrate surface 12a such that a uniform exposed molten metal layer is formed on the substrate surface at the onset of spray casting is shown by comparing surface treatments I, III and IV. It is apparent that the boronizing treatment with subsequent in-situ development of the molten layer on the substrate surface at the onset of spray casting results in better metallurgical diffusion bond joint properties than untreated substrates or boronized substrates where no exposed molten layer was subsequently developed on the substrate. Moreover, substrate surface texturing (e.g., knurling the substrate surface) prior to the boronizing surface treatment with development of the exposed molten layer yields further improvements in diffusion bond joint properties as illustrated by a comparison of surface treatments IV and V.

The criticality of developing the exposed molten layer on the substrate surface at the onset of spray casting in improving diffusion bond joint properties is confirmed by comparing surface treatments III, VI and VII. It is apparent that development of the exposed molten layer on the substrate surface at the onset of spray casting significantly improves the bond joint properties.

Another set of tests was conducted using so-called "dish" or "pseudo rotor" specimens D, FIG. 5, in lieu of the flat plate specimens described hereinabove. The "dish" specimen used is shown in FIG. 5 and had the

following dimensions, 5.25 inches OD×4.75 inches ID×1.75 inches depth (13.34 cm OD×12.07 cm ID×4.45 cm depth) with eight pairs of pins or spokes R,R' (simulating blades) extending in a radial direction from the dish sidewall S and spaced circumferentially apart around the dish sidewall S, FIG. 5. Four pairs of the pins R are 0.50 inch (1.27 cm) diameter while the other four pairs of smaller pins R' are 0.375 inch (0.95 cm) diameter in alternating sequence around the sidewall S. The pins are cast integrally with the sidewall of the dish specimen.

During low pressure, high velocity plasma spraying, each dish specimen D was positioned on a rotatable table with the sidewall S of the dish specimen extending vertically such that the cavity C could receive the spray cast deposit of LC Astroloy. Spray casting of the LC Astroloy was conducted using a spray gun oriented at 44 degrees to the dish side walls and at 46 degrees to the horizontal bottom and top lip of the dish specimen while the table was rotated. The spray gun was translated relative to the rotating dish specimen to insure build-up of a uniform deposit. All of the dish specimens were subjected to the vacuum cleaning treatment (a) and boronizing treatment (b) described above prior to placement in the spray chamber.

The dish specimens were subjected to low pressure plasma preheat (LPP), low temperature reverse clean (LTRAC) and high temperature reverse arc clean (HTRAC) procedures as described hereinabove for the plate specimens with care taken to insure a desired uniform temperature from the top to the bottom of the sidewall S during spray casting.

Table II sets forth stress rupture properties for the dish specimens. The stress rupture specimens shown in FIG. 7B were machined radially from the dish specimens D with the longitudinal axis of the stress rupture specimens coaxial to the axis of one of the large or small pins R,R' adjacent the top or bottom of the sidewall S such that bond joint J was normal to the longitudinal axis of the stress rupture specimen.

TABLE II

VPSD LC Astroloy to Cast Mar-M247 Pseudo Rotor (Dish Specimen) Bond Data									
Mar-M247 Surface Prep Method	Sample	Test Parameters	Individual Bar Data			Average Data			Fracture Comments
			Life (hrs)	% EL	% RA	$\bar{x}/\sqrt{n-1}$	$\bar{x}/\sqrt{n-1}$	$\bar{x}/\sqrt{n-1}$	
I Vapor Honed Only (No Boron, No Vac Clean, No Molten Layer, No Knurls)	2013	1400° F./80 ksi	31.1	1.9	2.1	25.9/4.6	1.6/0.5	1.4/0.7	Bond Line Failure
			20.2	1.0	0.5				Bond Line Failure
			27.7	1.4	1.9				Bond Line Failure
			24.9	2.0	1.2				Bond Line Failure
II Vacuum Cleaned Only (No Boron, No Molten Layer, No Knurls)	1929	1400° F./80 ksi	24.8	1.8	5.1	24.1/0.8	1.5/0.3	3.2/1.7	Bond Line Failure
			23.2	1.6	2.5				Bond Line Failure
			24.2	1.2	2.0				Bond Line Failure
III Boronized Only (No Molten Layer, No Knurls)	1947	1400° F./80 ksi	29.6	1.2	1.7	29.5/0.2	2.8/2.2	6.9/7.3	Bond Line Failure
			29.3	4.3	12.0				Parent Metal Failure
IV Knurling + Vac Cleaning + Boronizing + Molten Layer	2014	1400° F./80 ksi	50.6	5.6	16.8	64.5/18.6	5.1/1.4	16.2/1.2	Parent Metal Failure
			88.5	5.9	14.9				Parent Metal Failure
			48.9	3.0	15.5				Parent Metal Failure
			69.8	5.9	17.5				Parent Metal Failure
V Vacuum Clean + Boronized + Molten Layer (No knurls)	2016	1400° F./80 ksi	48.9	5.7	15.0	57.4/6.0	6.0/0.6	14.1/2.6	Parent Metal Failure
			57.3	5.5	10.2				Parent Metal Failure
			60.7	6.8	15.9				Parent Metal Failure
			62.5	6.0	15.2				Parent Metal Failure

Note:  
EL is elongation, RA is reduction in area,  $\bar{x}$  is an average,  $\sqrt{n-1}$  is sample standard deviation

From Table II, it can be seen by comparing surface treatments I through III and V that the combination of the vacuum cleaning treatment followed by the boronizing treatment with subsequent development of the molten layer on the substrate surface 12a at the onset of spray casting results in a significantly improved metallurgical diffusion bond joint as compared to the bond joints produced using the vapor honed treatment (Group I), the vacuum cleaning treatment (Group II) or the boronizing treatment (Group III) where no exposed molten layer was developed in-situ on the substrate surface at the onset of spraying. Moreover, by comparing surface treatment IV with the other treatments, it is apparent that initial substrate surface texturing (i.e., knurling the substrate surface) in combination with the vacuum cleaning treatment followed by the boronizing treatment with the subsequent development of the molten layer on the substrate surface at the onset of low pressure plasma spraying yielded further improvements in the properties of the metallurgical diffusion bond joint. Importantly, the Groups IV and V exhibited epitaxial grain growth across the diffusion bond joint after HIP and produced parent metal failures in the samples tested.

Table III reveals the results of 1400° F./80 KSI stress rupture tests of stress rupture specimens, FIG. 7B, machined from LC Astroloy/IN713LC dish specimens where LC Astroloy was spray cast in an IN713LC dish specimen, FIG. 5 which had been vacuum cleaned, boronized, preheated and HT RAC'ed to develop a molten layer at the onset of spray casting as explained hereinabove. After spray casting, these dish specimens were hot isostatically pressed at 2225° F. at 15 KSI for 4 h and then heat treated as described hereinabove for the plate specimens of Table I.

Six stress rupture bar specimens were tested from sample 2001 while four stress rupture bar specimens were tested from each of samples 2021 and 2022.

TABLE III

VPSD LC Astroloy To Cast IN713LC Pseudo Rotor (Dish Specimen) Bond Data 1400° F./80 KSI Stress Rupture Properties							
Sample	Life (hrs)		% EL		% RA		Fracture Comments
	$\bar{x}$	$\sqrt{n-1}$	$\bar{x}$	$\sqrt{n-1}$	$\bar{x}$	$\sqrt{n-1}$	
2001	40.7	3.6	7.1	0.9	15.3	1.9	All Parent Metal Failure
2021	62.0	7.2	8.1	0.7	14.3	3.8	All Parent Metal Failure
2022	56.0	1.7	8.4	0.4	19.4	1.7	All Parent Metal Failure

Note:  
EL is elongation, RA is reduction in area,  $\bar{x}$  is an average,  $\sqrt{n-1}$  is sample standard deviation

Again, subjecting the substrate surface to surface treatments (a) and (b) with the development of the uniform molten layer on the sidewall S (from top to bottom thereof) at the onset of spray casting in conjunction with subsequent hot isostatic pressing was effective to significantly enhance the structural integrity of the bond joint formed. The samples exhibited epitaxial grain growth across the diffusion bond joint after HIP and failures exclusively in the parent metal.

In practicing the present invention, the presence of epitaxial grain growth across the diffusion bond joint after HIP is preferred to further enhance bond structural integrity as evidenced by parent metal failures in the stress rupture tests.

As mentioned hereinabove, different substrate surface treatments have been discovered to have different effects on the diffusion bond joint properties of the spray cast specimens depending upon the similarity or

dissimilarity of the compositions of the substrate metal and the spray cast metal. The examples set forth hereinabove illustrate the effect for dissimilar compositions (i.e., LC Astroloy on investment cast Mar-M247 and IN713LC). The examples set forth hereinbelow illustrate the effect for similar compositions (i.e., LC Astroloy on LC Astroloy).

#### Testing Of Similar Compositions

In these tests, the substrate comprised a flat, square plate of nominal 2 inches (5 cm) width, 2 inches (5 cm) length and  $\frac{1}{4}$  inch (1.9 cm) thickness. The LC Astroloy substrate plate was formed by spray casting and hot isostatic pressing, but not bonding to any other substrate, under the same conditions as described hereinabove for the specimens. Specimens were prepared to investigate the effect of vacuum cleaning of the substrate surface on the structural integrity of the bond joint of the structural spray cast specimen. The vacuum cleaning treatment (as well as preheating and reverse arc cleaning) used to prepare the specimens was similar to that set forth above for the plate specimens of dissimilar composition. The vacuum cleaned specimens were compared against similar specimens which were vapor honed prior to preheating and reverse arc cleaning. The LC Astroloy was spray cast onto the LC Astroloy substrate plate to a thickness of about  $\frac{1}{4}$  inch (1.9 cm) using the same technique employed for spray casting the Mar-M247 on LC Astroloy.

After cooling, the spray cast preforms were hot isostatically pressed at 2165° F. and 25 KSI for 4 hours. Thereafter, the preforms were subjected to the same heat treatment described above for the plate specimens of dissimilar composition.

Table IV sets forth 1400° F./80 ksi stress rupture test results for the surface treatments investigated. The configuration of the stress rupture specimens is shown in FIG. 7A.

TABLE IV

VPSPD LC Astroloy to VPSPD LC Astroloy Flat Plate Bond Data									
Astroloy Surface Prep Method	Sample ID	Test Parameters	Individual Bar Data			Average Data			Fracture Comments
			Life (hrs)	% EL	% RA	$\bar{x}/\sqrt{n-1}$	% EL $\bar{x}/\sqrt{n-1}$	% RA $\bar{x}/\sqrt{n-1}$	
Vapor Honed Only (No Boron, No Vac Cleaning, No Molten Layer, No Kauris)	1899	1400° F./80 ksi	1.6	0.7	2.7	10.6/6.2	1.3/0.5	1.6/0.9	Planar Interface
			15.0	1.3	1.2				Planar Interface
			11.9	1.3	1.8				Planar Interface
			14.0	1.8	0.7				Planar Interface
Vacuum Cleaned Only (No Boron, No Molten Layer, No Kauris)	1927	1400° F./80 ksi	59.1	8.8	7.1	57.9/1.4	8.5/0.5	10.5/6.0	Bond Failure
			56.4	8.8	17.4				Parent Metal
			58.4	8.0	6.9				Bond Failure

Note:  
EL is elongation, RA is reduction in area,  $\bar{x}$  is an average,  $\sqrt{n-1}$  is sample standard deviation

Table IV demonstrates that the structural integrity of the bond joint between similar compositions of the substrate metal and the spray cast deposit can be enhanced by applying the vacuum cleaning surface treatment to the substrate surface prior to metal spray casting. The improvement with the vacuum cleaning treatment alone is believed to be due to the removal from the plate surface of certain tramp elements (mentioned hereinabove) which are deleterious to formation of a satisfactory metallurgical diffusion bond joint; i.e., a metallurgical diffusion bond joint which does not exhibit failure solely along the joint.

In summary, the enhancement of diffusion bond joint integrity of structural spray cast articles as measured by

stress rupture tests can be significantly improved by the application of the above discussed surface treatment processes (a)-(d) to the substrate 10 prior to deposition of the spray cast metal 11 and metallurgical diffusion bonding. In addition, the invention recognizes that the compositional difference between the materials of the substrate and the spray cast will impact the surface treatment processes necessary to enhance the bond joint integrity.

Although this invention has been shown and described with respect to a preferred embodiment, it will be understood by those skilled in the art that various changes in form and detail thereof may be made without departing from the spirit and scope of the claimed invention.

#### We claim:

1. In a method of making a structural article having a diffusion bond joint between a solid metal substrate constituting a first structural component of the article having selected mechanical properties and a solidified spray cast deposit thereon constituting a second structural component of the article having different mechanical properties, the improvement for increasing the structural integrity of the bond joint in sustaining a load across the joint, comprising the steps of:

- providing the solid metal substrate with a surface for receiving the deposit,
- heating said surface in the presence of a fluxing and melting point depressant agent at said surface to form an exposed in-situ liquid layer on said surface at the onset of plasma spraying of molten metal thereon,
- spraying the molten metal initially onto the exposed liquid layer to build-up the deposit on said surface, and
- diffusion bonding the deposit and the substrate to form said structural article.

2. The method of claim 1 wherein the fluxing and

melting point depressant agent is present at said surface prior to heating in step (b).

3. The method of claim 2 wherein the fluxing and melting point depressant agent comprises a boron-bearing diffusion layer at said surface.

4. The method of claim 1 wherein said surface is heated in step (b) by impinging a thermal plasma thereon.

5. The method of claim 4 wherein said surface is cleaned by reverse arc cleaning after impinging the thermal plasma thereon and immediately prior to the

onset of spraying of the molten metal onto said liquid phase.

6. The method of claim 4 or 5 wherein the substrate is a nickel base superalloy heated to at least about 2000° F.

7. The method of claim 1 including hot isostatically pressing the deposit and the substrate in step (d) to effect diffusion bonding therebetween.

8. The method of claim 7 including effecting epitaxial grain growth across the diffusion bond between said deposit and said substrate.

9. The method of claim 2 wherein said surface is vacuum cleaned prior to providing the melting point depressant at said surface, said surface being vacuum cleaned by exposing said surface at elevated temperature to a vacuum of at least about  $10^{-4}$  torr.

10. The method of claim 2 including knurling said surface prior to providing the melting point depressant at said surface.

11. The method of claim 1 wherein the solid metal substrate and the molten metal have different compositions.

12. The method of claim 1 wherein the solid metal substrate is provided as a bladed component of a turbine or compressor rotor and the solidified spray cast deposit is provided as a hub of the turbine or compressor rotor.

13. In a method of making a structural, multi-property article having a diffusion bond joint between a metal substrate constituting a first structural component of the article having selected mechanical properties and a solidified spray cast deposit thereon constituting a second structural component of the article having different mechanical properties, the improvement for increasing the structural integrity of the bond joint in sustaining a load across the joint under elevated temperature conditions without exhibiting failure solely in said joint, comprising the steps of:

- (a) providing the solid metal substrate with a surface for receiving the deposit,
- (b) providing a fluxing and melting point depressant agent at said surface,
- (c) heating said surface with the fluxing and melting point depressant agent at said surface to form an exposed in-situ liquid layer on said surface at the onset of spraying of molten metal thereon,
- (d) spraying the molten metal onto the exposed in-situ liquid layer to build-up the deposit on said surface, and
- (e) diffusion bonding the deposit and the substrate to form said structural article.

14. The method of claim 13 wherein the fluxing and melting point depressant agent comprises a boron-bearing layer at said surface.

15. The method of claim 13 wherein said surface is heated in step (c) by impinging a thermal plasma thereon.

16. The method of claim 15 wherein said surface is cleaned by reverse arc cleaning after impinging the thermal plasma thereon and immediately prior to the onset of spraying of the molten metal onto said liquid phase.

17. The method of claim 15 or 16 wherein the substrate is a nickel base superalloy heated to at least about 2000° F.

18. The method of claim 13 including hot isostatically pressing the deposit and the substrate in step (d) to effect diffusion bonding therebetween.

19. The method of claim 18 including effecting epitaxial grain growth across the diffusion bond between said substrate and said deposit.

20. The method of claim 13 wherein said surface is vacuum cleaned prior to providing the melting point depressant at said surface, said surface being vacuum cleaned by exposing said surface at elevated temperature to a vacuum of at least about  $10^{-4}$  torr.

21. The method of claim 13 wherein the metal substrate and the spray deposit have different compositions.

22. The method of claim 13 wherein the substrate comprises a single crystal metal member.

23. The method of claim 13 wherein the substrate comprises a directionally solidified columnar grain metal member.

24. The method of claim 13 wherein the substrate comprises an equiaxed grain member.

25. The method of claim 13 wherein the deposit has a low cycle fatigue resistant microstructure and the substrate has a creep resistant microstructure.

26. The method of claim 25 wherein the deposit has a fine grain microstructure.

27. The method of claim 13 including knurling the surface prior to step (b).

28. In a method of making a structural, multi-alloy, rotary article having a rotational axis and a diffusion bond joint between a creep resistant superalloy substrate constituting a first peripheral structural component of the article and a low cycle fatigue resistant solidified spray cast superalloy deposit constituting a second central structural component of the article, the improvement for increasing the structural integrity of the bond joint in sustaining a radial load across the joint under elevated temperature creep conditions without exhibiting failure solely in said joint, comprising the steps of:

- (a) providing the superalloy substrate with a surface of revolution relative to said axis for receiving the deposit,
- (b) providing a fluxing and melting point depressant agent at said surface,
- (c) heating said surface with the fluxing and melting point depressant agent at said surface and reverse arc cleaning the heated surface to form an exposed in-situ liquid layer on the surface at the onset of spraying of molten metal thereon,
- (d) spraying the molten metal onto the exposed in-situ liquid layer to build-up said superalloy deposit on said surface, and
- (e) diffusion bonding the deposit and the substrate to form said structural article.

29. The method of claim 28 wherein the substrate is a single crystal superalloy member.

30. The method of claim 28 wherein the substrate is a directionally solidified columnar grain superalloy member.

31. The method of claim 28 wherein the substrate is an equiaxed grain superalloy member.

32. The method of claim 28 including effecting epitaxial grain growth across the diffusion bond formed in step (e).

33. The method of claim 28 wherein the substrate is cast to have the surface of revolution.

34. The method of claim 33 wherein the substrate is cast to have a cylindrical surface of revolution.

35. In a method of making a multi-alloy bladed turbine or compressor rotor having a rotational axis and a

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diffusion bond joint between a creep resistant superalloy bladed ring and a low cycle fatigue resistant solidified spray cast superalloy hub, the improvement for increasing the structural integrity of the bond joint in sustaining a radial load across the joint under elevated temperature creep conditions without exhibiting failure solely in said joint, comprising the steps of:

- (a) casting the superalloy bladed ring to have a surface of revolution relative to said axis for receiving the deposit,
- (b) providing a fluxing and melting point depressant agent at said surface,
- (c) eating said surface with the fluxing and melting point depressant agent at said surface to form an exposed in-situ liquid layer uniformly across the surface at the onset of spraying of molten metal thereon,
- (d) spraying the molten metal onto the exposed in-situ liquid layer to build-up said superalloy deposit on said surface, and
- (e) diffusion bonding the deposit and the substrate to form said structural article.

36. In a method of making a structural article having a diffusion bond joint between a solid metal substrate constituting a first structural component of the article having selected mechanical properties and a solidified spray cast deposit thereon constituting a second structural component of the article having different mechanical properties, the improvement for increasing the structural integrity of the bond joint in sustaining a load across the joint, comprising the steps of:

- (a) providing the solid metal substrate with a performed surface for receiving the deposit,
- (b) vacuum cleaning the substrate surface at elevated temperature,
- (c) boronizing the vacuum cleaned substrate surface,
- (d) plasma heating the boronized substrate surface,

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(e) reverse arc cleaning the preheated, boronized substrate surface and forming an exposed in-situ liquid layer on said surface at the onset of plasma spraying of molten metal thereon,

(f) spraying the molten metal initially onto the exposed liquid layer to build-up the deposit on said surface, and

(g) diffusion bonding the deposit and the substrate to form said structural article.

37. In a method of making a structural, multi-alloy, rotary article having a rotational axis and a diffusion bond joint between a creep resistant superalloy substrate constituting a first peripheral structural component of the article and a low cycle fatigue resistant solidified spray cast superalloy deposit constituting a second central structural component of the article, the improvement for increasing the structural integrity of the bond joint in sustaining a radial load across the joint under elevated temperature creep conditions without exhibiting failure solely in said joint, comprising the steps of:

- (a) providing the superalloy substrate with a performed surface of revolution relative to said axis for receiving the deposit,
- (b) vacuum cleaning the substrate surface at elevated temperature,
- (c) boronizing the vacuum cleaning substrate surface,
- (d) plasma heating the boronized substrate surface,
- (e) reverse arc cleaning the preheated, boronized substrate and forming an exposed in-situ liquid layer on the surface at the onset of spraying of molten metal thereon,
- (f) spraying the molten metal onto the exposed in-situ liquid layer to build-up said superalloy deposit on said surface, and
- (g) diffusion bonding the deposit and the substrate to form said structural article.

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